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A Gallium(III) Halide Complex Containing 5-Coordinate Gallium $GaCl_3 \cdot 1,4$-dioxane

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$GaCl_3 \cdot 1,4$-dioxane has been shown by X-ray diffraction to contain 5-coordinate gallium. The crystal structure, which is isomorphous with $TlBr_3 \cdot 1,4$-dioxane [1], consists of infinite chains of distorted planar $GaCl_3$ units bridged by dioxane chairs.

Complexes of stoichiometry $MX_3 \cdot 2L$ (X = halogen, L = monodentate ligand) are well known for all of the metallic elements of group(III). Distorted trigonal bipyramidal geometry has been confirmed in many complexes of Al, In, Tl *e.g.* see references [2–4]. There is a dearth of structural information available for gallium compounds and further in two compounds whose structures are known *i.e.* $GaCl_3 \cdot 2$pyridine [5] and $GaCl_3 \cdot 2,2'$-bipyridyl [6] the expected 5-coordination is not observed and the structures contain 4 and 6-coordinate ions. On the other hand spectroscopic studies on $GaCl_3 \cdot 2$trimethylamine [7] have been interpreted in terms of 5-coordinate gallium but this remains to be confirmed by X-ray analysis.

TABLE I. Fractional Atomic Coordinates ($\times 10^4$).

	x	y	z
Ga	0*	454(2)	250*
Cl(1)	0*	3779(4)	250*
Cl(2)	1992(2)	−1094(3)	3458(1)
O(1)	147(4)	318(8)	1041(5)
C(1)	894(7)	−1432(11)	−48(5)
C(2)	384(8)	−1724(10)	721(5)

*Constrained.

5-coordinate gallium has been confirmed however in complexes containing less halogen: *e.g.* in chloro(dimethyl)-1,10-phenanthrolinegallium(III) [8] and N,N′-ethylenebis(salicylideneimato)chlorogallium(III) [9]. In these cases the ligand has more than one donor site in close proximity and 5-coordination may be a consequence of this.

This paper describes the crystal structure of $GaCl_3 \cdot 1,4$-dioxane; 5-coordination appeared likely here in view of our recent crystal structure determinations on the Al and Tl analogues [1, 10].

$GaCl_3 \cdot 1,4$-dioxane was prepared by condensing dry 1,4-dioxane on to the trihalide *in vacuo*. On removal of the excess ligand a white powder remained which was recrystallized from dry acetonitrile

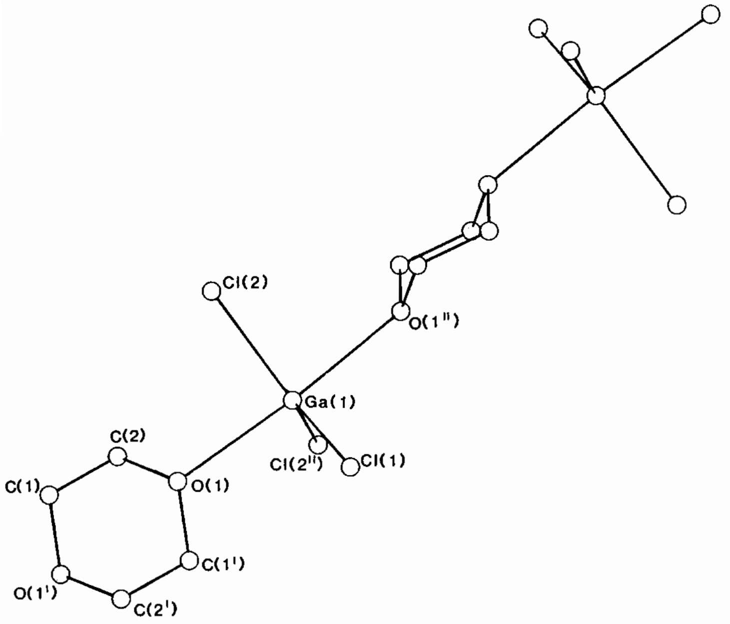

Fig. 1. The structure of $GaCl_3 \cdot 1.4$-dioxane. Bond distances: Ga–Cl(1), 2.152(3); Ga–Cl(2), 2.159(2); Ga–O, 2.210(4) Å. Bond angles: Cl(1)–Ga–Cl(2), 117.6(1); Cl(2)–Ga–Cl(2′), 124.8(1)°.

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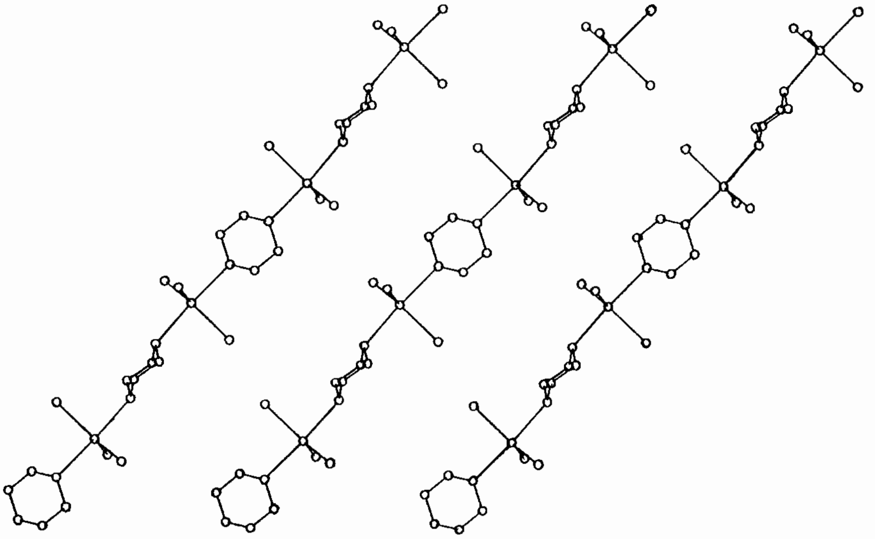

Fig. 2. Arrangement of chains within the unit cell.

to give crystals suitable for X-ray analysis. The structure was solved by a single crystal X-ray study. *Crystal Data* (20 °C) for [$GaCl_3 \cdot 1,4$-dioxane] : monoclinic, space group $C2/c$, $a = 10.85(1)$, $b = 19.62(2)$, $c = 11.18(1)$ Å, $\beta = 123.2(1)$, $\mu = 3.76$ mm^{-1}. Intensity measurements were made on a Stoe STADI-2 diffractometer using MoKα radiation. 935 reflections were measured and after elimination of those for which $I < 3\sigma(I)$ there remained 906 unique reflections which were used in the final refinement. The structure was solved using MULTAN [11] and SHELX [12] refined anisotropically for Ga, C and O; currently the R value is 0.0446. Fractional atomic coordinates are given in Table I.*

The crystal structure consists of distorted planar $GaCl_3$ units bridged by dioxane molecules, in the chair conformation, to form infinite chains parallel to the c-axis. Distorted trigonal bipyramidal geometry is observed around gallium (Figs. 1 and 2). The structure is isomorphous with $TlBr_3 \cdot 1,4$-dioxane [1] and similar to $AlCl_3 \cdot (1,4\text{-dioxane})_2$ [10]. The Ga–Cl distances (Ga–Cl 2.152(3), 2.159(2) Å) are significantly shorter and the Ga–O (2.206(6) Å) longer than in other 5-coordinate compounds (Ga–Cl 2.190(5)–2.223(5) Å; Ga–O 1.845(5)–1.967(5) Å) [9]. This may be ascribed to the weakness of the dioxane ligand towards $GaCl_3$. A previous NQR investigation has shown that for 1:1 $GaCl_3$ adducts the ionicity of the Ga–Cl bond, and hence the bond distance, increases with ligand donor strength [13].

We have previously reported the structure of the Ga–Ga bonded complex $Ga_2Cl_4 \cdot 2$dioxane [14]. It should be noted that in this complex the ligand is monodentate and the Ga–O distance is considerably reduced (2.021(5), 2.033(5) Å).

The gallium halides thus provide a number of interesting coordination modes with the ligand dioxane. A further boat form has been reported in $Ga(\text{dioxane})_2Cl$ [15] but this structure is of low accuracy and should be repeated.

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*Lists of structure factors are available on request from the authors.