

## A Distorted Octahedral Gallium Complex

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**Summary** The compound supposed to be  $\text{GaCl}_3 \cdot \text{bipy}$  has been shown to be a dimer of true formula  $[\text{GaCl}_2(\text{bipy})_2]^+ [\text{GaCl}_4]^-$ .

THE existence of a metal atom in two different configurations in the same crystal is unusual and rare. In our crystal structure study of  $\text{GaCl}_3 \cdot \text{bipy}$  (bipy = 2,2'-bipyridyl), the gallium atom is found in the anionic tetrahedral configuration  $\text{GaCl}_4^-$  and the cationic form  $\text{GaCl}_2(\text{bipy})_2^+$ , the first octahedral complex of gallium.

Colourless crystals, from acetone, were studied by X-ray diffraction, using  $\text{Cu-K}\alpha$ -radiation:  $\text{C}_{20}\text{H}_{16}\text{N}_4\text{Cl}_6\text{Ga}_2$ ,  $M = 664.5$ ; orthorhombic,  $a = 14.900(3)$ ,  $b = 12.469(2)$ ,  $c = 13.561(2)$  Å,  $U = 2519.5$  Å<sup>3</sup>,  $D_m = 1.750$  g./cm.<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.752$  g./cm.<sup>3</sup>; space group  $Pccn$  (No. 56).

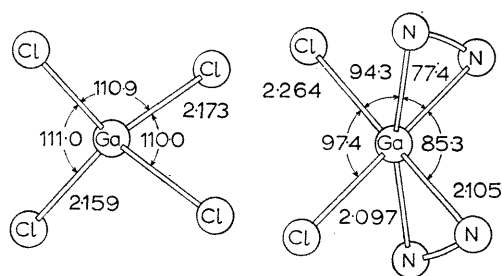
The intensities of 2275 (1907 non-zero) independent reflections ( $2\theta \leq 135.0^\circ$ ) were measured with a G.E. diffractometer. The structure has been solved by the heavy-atom method and refined by least-squares methods using anisotropic thermal parameters to an  $R$  of 6.2%.

Our analysis shows the structure to be 'ionic', with the Ga atoms in  $[\text{GaCl}_2(\text{bipy})_2]^+ [\text{GaCl}_4]^-$  in special positions on two-fold axes. The immediate co-ordination about the two gallium atoms is illustrated in the Figure. The Ga-Cl distance of 2.264(2) Å in the octahedral cation is significantly longer than the average value of 2.166(3) Å found in the tetrahedral anion, in agreement with an increase in bond radius with co-ordination number. The *cis*-configuration of the cation was unexpected since the *trans*-configuration

was favoured by the i.r. spectra studies,<sup>1,2</sup> which may require a re-interpretation.

A comparison of the Ga-Cl and Ga-N distances reveals that the difference between the two bond lengths is only 0.159 Å while the difference between the Cl and N bond radius is about 0.29 Å. Therefore, either the Ga-Cl bond is shorter or the Ga-N bond is longer than a single bond. Unfortunately, the lack of structural data on gallium compounds precludes a definitive answer at this time.

The octahedral configuration in the  $[\text{GaCl}_2(\text{bipy})_2]^+$  cation together with the recent studies on  $[(\text{C}_2\text{H}_5)_4\text{N}]_2\text{InCl}_5^3$  and  $\text{InCl}_3[\text{P}(\text{C}_6\text{H}_5)_3]_2^4$  have demonstrated the existence of higher co-ordination numbers for both Ga and In.



Distances and angles in the tetrachlorogallate anion (upper molecule) and the *cis*-dichlorobis-(2,2'-bipyridyl)gallium(III) cation (lower molecule).

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