A *trans*-Effect in Gallium Complexes: the Crystal Structure of Trichloro-(2,2′,2″-terpyridyl)gallium(III)

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Summary The molecular structure of GaCl$_3$·terpyridyl is interpreted in terms of a *trans*-effect in d^{10} complexes which influences the M–X (X = halogen) distances and is instrumental in determining the geometry of the metal–halide complexes.

THE first structurally characterized octahedral complex ion of gallium, dichlorobis(bipyridyl)gallium(III), has a *cis*-configuration with anomalous Ga–Cl and Ga–N bond lengths.[1] A related complex, trichloroterpyridylgallium(III), GaCl$_3$(terpy), where (terpy) = 2,2′,2″-terpyridyl has been prepared and characterized by spectral and *X*-ray diffraction studies. Although the spectral results favoured a five-co-ordinate formulation, the *X*-ray crystal structure study revealed an octahedral structure. The molecular dimensions demonstrate that the Ga–Cl bond length is dependent on the nature of the ligand *trans* to the chlorine. These results also suggest an explanation for the *cis*-geometry of GaCl$_2$(bipy)$_2^+$ and illustrate the dangers inherent in the elucidation of molecular structure by far-i.r. spectroscopy.

Colourless crystals of GaX$_3$(terpy) (X = Cl, Br, or I) were obtained from the reaction of GaX$_3$ and (terpy) in ethanol. A simple interpretation of the far-i.r. spectra of GaX$_3$(terpy) (X = Cl, ν 342 vs, 322 m, 268 vs, 220 s; X = Br, ν 333 m, 305 s, 285 vs, 270 vs, 210 m; X = I, ν 324 m, 267 m, 253 s, 228 vs, 212 m cm^{-1}) in terms of bond-stretching co-ordinates suggests ν(Ga–Cl) at 342 cm^{-1} and ν(Ga–N) at 268 cm^{-1}. The structure Ga(terpy)$_2^{3+}$GaCl$_6^{3-}$ can be eliminated† but one cannot readily distinguish between a pentaco-ordinated GaCl$_2$(terpy)$^+$ or octahedral GaCl$_3$(terpy). A comparison with GaCl$_2$(bipy)$_2^+$ [ν(Ga–Cl) 302 cm^{-1}] and GaCl$_3$(py) [ν(Ga–Cl) 392 cm^{-1}] favoured the pentaco-ordinated species since ν(M–Cl) frequencies generally increase with a decrease in the co-ordination number of the metal ion.

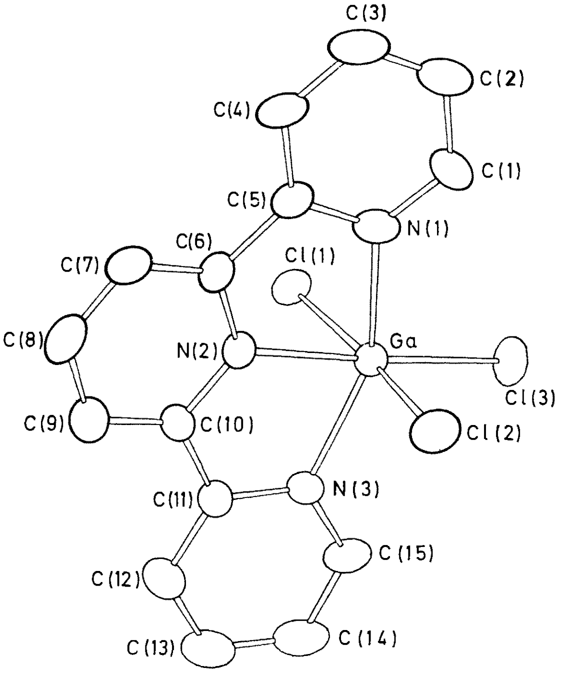

FIGURE. *A view of trichloroterpyridylgallium*(III) *indicating the geometry and atomic numbering.*

Crystal data: C$_{15}$H$_{11}$N$_3$Cl$_3$Ga, M 409·1, monoclinic crystals, space group $P2_1/c$ (No. 14), $a = 8{\cdot}324(3)$, $b = 14{\cdot}120(8)$, $c = 14{\cdot}223(5)$ Å, $\beta = 110{\cdot}77(2)°$, $U = 1575{\cdot}1$ Å^3, $D_m = 1{\cdot}702$ g/cm^3, $Z = 4$, $D_c = 1{\cdot}725$ g/cm^3.

The intensities of 2820 (2174 non-zero) independent reflections ($2\theta \leqslant 135°$ for Cu radiation) were measured with a G.E. diffractometer. The structure was solved by the heavy-atom method and refined by least-squares methods using anisotropic thermal parameters to an R of 0·063.

The molecular geometry and atomic numbering are illustrated in the Figure. The co-ordination about the gallium atom is octahedral, not pentaco-ordinated as expected. The pertinent Ga–ligand distances are Ga–Cl(1) 2·403(2), Ga–Cl(2) 2·329(3), Ga–Cl(3) 2·235(3), Ga–N(1) 2·115(6), Ga–N(2) of 2·034(7), and Ga–N(3) 2·110(6) Å.

The distances in the terpyridyl group are normal, with an average C–C(ring) distance of 1·382, C–C(inter-ring) distance average of 1·471, and the C–N bond average of 1·337 Å. The Ga–N(1) and Ga–N(3) distances are identical with the average value of 2·103(6) Å reported[1] for GaCl$_2$(bipy)$_2^+$ and are close to the values 2·097(6) and 2·182(5) Å found in GaH·EDTA·H$_2$O.[2] (EDTA = ethylenediaminetetra-acetate). Since the Ga–N distance is approximately constant in all three compounds, a Ga–N single bond is assumed to be about 2·10 Å.

The most striking feature of the structure is that the three Ga–Cl bonds are all significantly different. The difference between the *trans* Ga–Cl(1) and Ga–Cl(2) bonds appears to be a steric effect resulting from the restricted geometry of the terpyridyl ligand.‡ The difference between the Ga–Cl(3) bond distance and the other two Ga–Cl bonds is the result of a *trans*-effect; namely, a Ga–Cl *trans* to a Ga–N is shorter than a Ga–Cl *trans* to Ga–Cl. The Ga–Cl(3) distance agrees well with the Ga–Cl distance of 2·264(2) Å found in *cis*-GaCl$_2$(bipy$_2^+$). If we assume that a Ga–N bond distance of 2·10 Å represents a single bond, then the Ga–Cl(1) distance is also a single bond but the Ga–Cl(2) and Ga–Cl(3) bonds are stronger than a single bond. The alternative suggestion that the Ga–Cl(3) is a normal single bond and the other bonds are weaker is not consistent with the GaH·EDTA·H$_2$O structure.[2] Tetrahedral zinc chloride–nitrogen base adducts also show

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† ν_3 for the unknown GaCl$_6^{3-}$ ion should be below 300 cm^{-1}.

‡ The nonbonded contacts Cl(1)–N(1) 3·174(8), Cl(1)–N(2) 2·997(7), Cl(1)–N(3) 3·172(7), Cl(2)–N(1) 3·169(7), Cl(2)–N(2) 3·119(6), and Cl(2)–N(3) 3·118(7) Å support this view.

variable Zn–X (X = halogen) bonds but the Zn–N bonds are constant.[3] The conclusion is that electronic effects in d^{10} metal complexes influence the M–X bonds, with the M–N bonds remaining nearly constant. Furthermore, the *cis*-configuration observed in the $GaCl_2(bipy)_2^+$ complex is simply a manifestation of this *trans*-effect since stronger Ga–Cl bonds will be formed if the Cl atoms are *cis* to each other.

The *X*-ray results for $GaCl_2(bipy)_2^+$ and $GaCl_3$(terpy) also illustrate the inadequacies of far-i.r. spectroscopy for structural deductions. Although this technique has been widely used recently,[4] the correct structures for the relatively simple complexes $GaCl_3$(bipy) and $GaCl_3$(terpy) could not be deduced from the far-i.r. data. In the latter complex, the presence of different Ga–Cl bonds, one of which was stronger than in $GaCl_2(bipy)_2^+$, could account for the unexpected ν(Ga–Cl) frequency of 343 cm^{-1}. Moreover, only one readily distinguishable ν(Ga–Cl) mode was found compared to the three ν(Ga–Cl) ($2a_1 + b_2$) expected for a *trans*-MX_3L_3 skeleton. In $GaCl_3$(bipy) the accidental degeneracy of the two ν(Ga–Cl) modes expected for a *cis*-cation led to the assumption of a *trans*-geometry. The obvious conclusion is that i.r. results are best interpreted with a knowledge of the molecular structure determined by *X*-ray studies.

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