Synthesis and Structure of a Five-co-ordinate Gallium Complex: Chlorobis-(8-hydroxy-2-methylquinolinato)gallium(III)

By K. DYMOCK and GUS J. PALENIK*

(*Department of Chemistry, University of Florida, Gainesville, Florida* 32611)

Summary Synthesis of trigonal bipyramidal chlorobis-(8-hydroxy-2-methylquinolinato)gallium(III) and characterization by i.r., m.s., and *X*-ray diffraction techniques reveals a rare example of five-co-ordination resulting from a combination of steric and solvation effects.

THE co-ordination chemistry of 8-hydroxy-2-methylquinoline is dominated by steric considerations.[1,2] An example of these steric effects is shown by the Ga^{III} system, where either tris-(8-hydroxy-2-methylquinolinato)gallium(III), (I), or chlorobis-(8-hydroxy-2-methylquinolinato)gallium(III), (II), can be obtained depending on the reaction conditions. In water, the Ga^{III} ion reacts with 8-hydroxy-2-methylquinoline to yield (I), while in absolute methanol, $GaCl_3$ reacts with 3 equiv. of the sodium salt of 8-hydroxy-2-methylquinoline to give (II). The latter compound is the first five-co-ordinate Ga^{III} complex to be prepared and fully characterized. This unusual difference in reactivity appears to be due to the nature of the solvation of the Ga^{III} species in solution.

The reaction of anhydrous $GaCl_3$ with the sodium salt of 8-hydroxy-2-methylquinoline in absolute methanol gives green crystals, (II), which are different in colour from the product, (I), obtained in water.[2] Analytical data confirmed the existence of two compounds. Mass spectra give the highest m/e peaks for (I) at 544 and for (II) at 421, corresponding to the values calculated for the ^{69}Ga species. The far i.r. spectra for (I) and (II) are strikingly different. Only (II) gives a large absorption at 364 cm^{-1}, which is attributed to ν (Ga–Cl) since the peak is midway between the ν(Ga–Cl) for tetrahedral species at 410 cm^{-1} and for octahedral species at 300 cm^{-1}.[3] The experimental evidence suggested a five-co-ordinate gallium complex and therefore an X-ray study was undertaken to confirm this hypothesis.

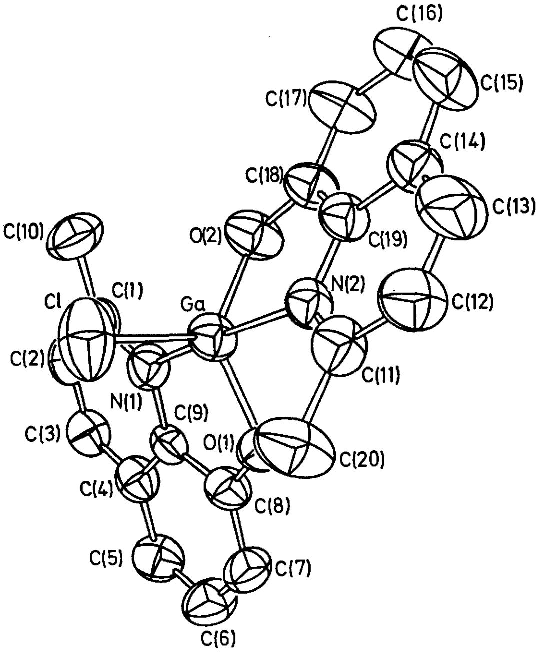

FIGURE. A view of chlorobis-(8-hydroxy-2-methylquinolinato)-gallium(III) showing the atomic numbering and the thermal ellipsoids. The pertinent angles are: Cl–Ga–O(1) 113·6(1); Cl–Ga–O(2) 120·4(2); O(1)–Ga–O(2) 125·9(2); and N(1)–Ga–N(2) 169·1(2)°.

Crystal data: GaClC$_{20}$H$_{16}$N$_2$O$_2$, $M = 421{\cdot}5$, monoclinic, space group $I\,2/a$, $a = 25{\cdot}232(11)$, $b = 9{\cdot}555(2)$, $c = 15{\cdot}165(4)$ Å, $\beta = 93{\cdot}04(3)°$, $D_m = 1{\cdot}53$ g cm^{-3}, $Z = 8$ $D_c = 1{\cdot}535$ g cm^{-3}, $R = 0{\cdot}052$ for 1839 observed reflections measured using graphite-monochromatized Mo-K_α radiation with a P$\bar{1}$ Diffractometer.

The molecular geometry and atomic numbering are shown in the Figure. The gallium atom is the centre of a trigonal bipyramid formed by the chlorine atom and the two oxygen and two nitrogen atoms of the ligands. The Ga–N distances [2.108(5) and 2·104(5) Å] are identical to the values found in octahedral gallium complexes[4] which range from 2·083(10) to 2·115(6) Å.† The similarity of the Ga–N distances is unexpected since bond distances usually vary with co-ordination number. In contrast, the Ga–Cl distance of 2·190(2) Å in (II) is shorter than the Ga–Cl distances in octahedral complexes which show a wide range of values from 2·235(3) to 2·403(3) Å. An analysis of the available structural data suggests that the Ga–N distances are virtually constant, while the Ga–Cl distances are determined by non-bonded interactions. Therefore, the Ga–Cl distances will be dependent upon ligand geometry, as well as on the nature of the other atoms in the co-ordination sphere. A similar observation may be made for copper(II) chloride complexes with oxygen donors.[5] Therefore, the concept and use of "single-bond radii" is not generally valid.

Since (II) is soluble in methanol, the reaction medium, the stability of this unusual complex does not appear to be a solid state effect. Although (II) fails to react with the sodium salt of 8-hydroxy-2-methylquinoline to give a tris species, a slow reaction with AgNO$_3$ does take place. The reaction is very slow, which suggests that (II) does not exist as the four-co-ordinate cation in methanol. The most reasonable explanation for these observations is a kinetic one based on the fact that nucleophilic attack is sterically hindered. The inertness of (II) is surprising since Ga$^{\text{III}}$ species are generally labile[6]. However, the fact that the larger InCl$_3$ species in methanol gives the tris complex[7] supports the kinetic arguments. Our results demonstrate that the reaction of GaCl$_3$ in methanol with the sodium salt of the ligand proceeds in a stepwise manner and that (II) represents the rare example of a five-co-ordinate reaction intermediate which can be isolated and characterized.[8]

We thank the U.S. Public Health Service, National Cancer Institute, for partial financial support of this research and the University of Florida Computing Center for a grant of computer time.

(*Received*, 10*th July* 1973; *Com.* 985.)

---

† The Ga–N distance of 2·034(7) Å to the central nitrogen of the terpyridine ring in GaCl$_3$(tpy) has not been included. The steric constraints of the terpyridine ligand does not permit all N atoms to be equidistant from the central metal.

[1] Y. Kushi and Q. Fernando, *J. Amer. Chem. Soc.*, 1970, **92**, 91.

[2] H. Irving, E. J. Butler, and M. F. Ring, *J. Chem. Soc.*, 1949, 1489.

[3] A. J. Carty, *Coordination Chem. Rev.*, 1969, **4**, 29.

[4] R. Restivo and G. J. Palenik, *J.C.S. Dalton*, 1972, 34; G. Beran, A. J. Carty, H. A. Patel, and G. J. Palenik, *Chem. Comm.*, 1970, 222; K. Dymock, G. J. Palenik, and A. J. Carty, *ibid.*, 1972, 1218.

[5] M. Mathew and G. J. Palenik *Inorg. Chim. Acta.*, 1971, **5**, 573.

[6] F. Basolo and R. G. Pearson, 'Mechanisms of Inorganic Reactions,' Wiley, New York, 2nd edn., 1967, p. 144.

[7] K. Dymock and G. J. Palenik, unpublished results.

[8] The question of five-co-ordinated species as reaction intermediates has been discussed recently by J. S. Wood, *Progr. Inorg. Chem.*, 1972, **16**, 227.