Preparation and Crystal Structure of a Novel Hydroxo-bridged Gallium Complex $[Ga_2(OH)_2Cl_2(C_{14}H_{17}N_3)_2]Cl_2,H_2O$

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Summary The first hydroxo-bridged octahedral gallium chloride complex has been isolated and characterized by both i.r. and *X*-ray diffraction techniques; the variability of the Ga–Cl distance in gallium chloride complexes is also demonstrated.

Crystal structure studies of trichloroterpyridine gallium(III),[1] $GaCl_3$(terpy), and the *cis*-dichlorobis-(2,2′-bipyridyl)-gallium(III) cation,[2] $GaCl_2(bipy)_2^+$, revealed that the Ga–N distances were virtually constant while the Ga–Cl distances varied widely in the two complexes. As an extension of these studies we prepared (MeMe′dpma)$GaCl_3$, where MeMe′dpma is methyl-(6-methyl-2-pyridylmethyl)(2-pyridylmethyl)amine for a comparison with the $GaCl_3$(terpy) complex. The crystalline complex which was isolated gave the correct C, H, and N analysis for (MeMe′dpma)-$GaCl_3$ but a subsequent *X*-ray analysis indicated that the compound was di-μ-hydroxo-bis[chloro{methyl-(6-methyl-2-pyridylmethyl)-(2-pyridylmethyl)amine}gallium(III)] chloride monohydrate. This represents the first structural evidence that the hydroxo-complexes which have been postulated as intermediates in the controlled hydrolysis of gallium trihalide adducts[3,4] can exist and can be isolated.

The reaction of MeMe′dpma[5] with $GaCl_3$ in reagent grade acetonitrile gave colourless crystals which, by analogy to the 2,2′,2″-terpyridyl reaction[6] was assumed to be $GaCl_3$(MeMe′dpma). After the *X*-ray analysis further study of the reaction indicated that a second compound analysing as $(GaCl_3)_2$(MeMe′dpma) could be obtained from carefully dried benzene or ether solutions of $GaCl_3$ by addition of MeMe′dpma. The i.r. and Raman spectra of the latter anhydrous compound indicated that both pyridine nitrogen atoms were co-ordinated and that the $GaCl_4^-$ ion was present. Hence the compound was formulated $[GaCl_2$(MeMe′dpma)$]^+GaCl_4^-$ or $[GaCl_2$(MeMe′dpma$]_2$ $(GaCl_4^-)_2$. Partial hydrolysis of $(GaCl_3)_2$(MeMe′dpma) in moist acetonitrile gave the hydroxo-bridged species $[Ga_2(OH)_2Cl_2$(MeMe′dpma)$_2]Cl_2H_2O$.

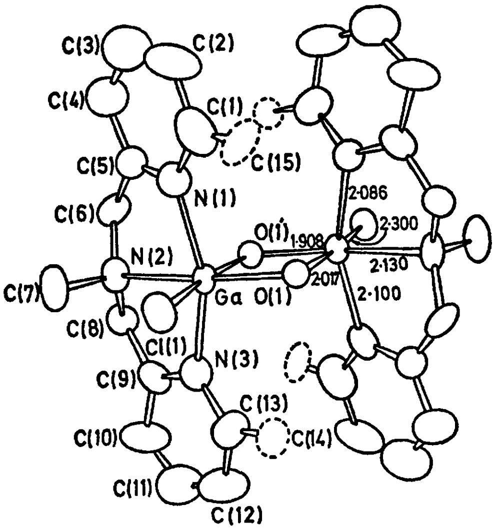

FIGURE. *A view of the di-μ-hydroxo-bis[chloro{methyl-(6-methyl-2-pyridylmethyl)-(2-pyridylmethyl)amine}gallium*(III)] *cation showing the atomic numbering and the average bond distances.*

Crystal data: $[Ga(Cl)(OH)(C_{14}H_{17}N_3)]_2^{2+}2Cl^-,H_2O$, triclinic crystals, space group $P\bar{1}$, $a = 13{\cdot}040(7)$, $b = 12{\cdot}284(7)$, $c = 11{\cdot}000(7)$ Å, $\alpha = 95{\cdot}28(2)$, $\beta = 84{\cdot}54(3)$, $\gamma = 97{\cdot}82(3)°$, $Z = 2$.

The structure analysis was based on 3161 diffractometer measured intensities. The Patterson function was interpreted on the basis of two crystallographically independent dimer units each possessing $\bar{1}$ symmetry. A Fourier synthesis phased on the gallium and chlorine atoms suggested that the bridging groups were oxygen atoms. Subsequent refinement of the structure by least-squares methods to a final *R* of 0·070 indicated the correctness of the structure and formulation.

The molecular geometry and atomic numbering are shown in the Figure. Although the ligand has only one methyl group attached to one pyridine ring, there appeared to be a disorder in the solid giving rise to methyl peaks at both positions. The distances shown in the Figure are average values from the two independent dimer units. The Ga–N(2) distances [2·132(9) and 2·127(9) Å] are both longer than the Ga–N(1) [2·100(10) and 2·099(9) Å] or Ga–N(3) [2·088(9) and 2·083(10) Å] distances. Whether this is an electronic or steric effect cannot be decided at this time. However, the Ga–N distances are very similar to the values found in *cis*-$GaCl_2(bipy)_2^+$ of 2·095(4) and 2·111(4) Å and in $GaCl_3$(terpy) of 2·115(6), 2·034(7), and 2·110(6) Å which again shows the approximately constant nature of the Ga–N distance. In contrast, the Ga–Cl distances [2·311(4) and 2·289(4) Å] appear to be significantly different from the values in *cis*-$GaCl_2(bipy)_2^+$ of 2·265(1) Å or in $GaCl_3$(terpy) of 2·403(2), 2·329(3), and 2·235(3) Å. We see that the concept of a constant Ga–Cl distance in octahedral gallium complexes is not valid. A similar effect has been observed in $CuCl_2L_2$ species with L = oxygen donor.[7]

The reaction of MeMe′dpma with $InCl_3$ or $TlCl_3$ in acetonitrile gives crystalline, non-ionic complexes of the type MCl_3(MeMe′dpma), with a *mer* octahedral configuration similar to the series of complexes MCl_3(terpy) (M = Al, Ga, In, or Tl).[6] The far-i.r. spectra of $[Ga_2(OH)_2X_2$(MeMe′dpma)$_2]^{2+}2X^-H_2O$ shows a strong band at 530 cm^{-1} for X = Cl and at 532 cm^{-1} for X = Br which is absent for the MX_3 (MeMe′dpma) complexes, M = In or Tl and X = Cl or Br and hence is due to $\nu(Ga–O)_{as}$. These bands should prove a useful diagnostic test for bridging hydroxo groups in six-coordinate gallium species.

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[1] G. Beran, A. J. Carty, H. A. Patel, and G. J. Palenik, *Chem. Comm.*, 1970, 222.

[2] R. Restivo and G. J. Palenik, *J.C.S. Dalton*, 1972, 341.

[3] E. Kinsella, J. Chadwick, and J. Coward, *J. Chem. Soc.* (*A*), 1968, 969 and references therein.

[4] B. N. Ivanov-Emin and Ya. I. Rabovik, *Zhur. neorg. Khim.*, 1959, **4**, 2228; see *Chem. Abs.*, 1960, **54**, 15062a.

[5] M. M. da Mota, S. M. Nelson, and J. Rodgers, *J. Chem. Soc.* (*A*), 1969, 2036.

[6] G. Beran, K. Dymock, H. A. Patel, A. J. Carty, and P. M. Boorman, *Inorg. Chem.*, 1972, **11**, 896.

[7] M. Mathew and G. J. Palenik, *Inorg. Chim. Acta*, 1972, **5**, 573.