X-Ray Structural Characterization of the Pyrazolyl-dideuteriogallane Dimer

By DAVID F. RENDLE, ALAN STORR,* and JAMES TROTTER
(*Department of Chemistry, University of British Columbia, Vancouver 8, B.C., Canada*)

Summary The tricyclic pyrazolyl-dideuteriogallane dimer $[N_2C_3H_3{\cdot}GaD_2]_2$ has been structurally characterized by a single crystal *X*-ray study; the six-membered $Ga(N{-}N)_2Ga$ ring is shown to be in the boat conformation.

As part of a continuing investigation[1] of the reactions of Group III compounds with ligands containing active hydrogen a number of pyrazolyl derivatives have been prepared containing aluminium and gallium moieties.[2] This report presents the first structural characterization of a member of the symmetrical dimeric class of compounds, $[N_2C_3H_3{\cdot}MR_2]_2$ (where M = B, Al, or Ga; R = H, D, Me, Et). Crystal structures of a number of related poly-(1-pyrazolyl)-borate transition-metal complexes have been reported previously,[3,4,5,6] and have in common *unsymmetrical* six-membered rings, $B(N{-}N)_2M'$ (where M' = Mo or Co), in pseudo-boat conformations.

The present gallane compound was prepared by reaction of equimolar amounts of pyrazole and trimethylamine-trideuteriogallane in benzene solution. Stoicheiometric amounts of trimethylamine and hydrogen deuteride were liberated and the gallane product, $[N_2C_3H_3{\cdot}GaD_2]_2$, isolated as a volatile solid. It was dimeric in benzene solution and gave a simple doublet (τ 2·69 p.p.m.; J 2·2 Hz) triplet (τ 4·14 p.p.m.; J 2·2 Hz) pattern for the pyrazolyl ring protons in the n.m.r. spectrum in deuteriobenzene, suggesting symmetrical bonding of these rings in the molecular unit. The compound analysed well for gallium and hydrolysable deuterium (Ga : D = 1 : 2) and readily sublimed to give colourless crystals. A suitable sample for *X*-ray study was positioned in a capillary tube under a nitrogen atmosphere in a glove box.

The crystals are orthorhombic, a = 11·518(2), b = 11·278(1), c = 8·267(1) Å, space group $Cmc2_1$; Z = 4. The

intensities of 545 (491 observed) reflexions with $2\theta \leqslant 135°$ were measured on a Datex-automated G.E. XRD6 diffractometer with Cu-K_α radiation ($\lambda = 1{\cdot}5418$ Å). The atomic positions were determined by Patterson and Fourier syntheses and refined by full-matrix least-squares methods using weights derived from counting statistics to $R = 0{\cdot}050$ for the observed reflexions. The hydrogen and deuterium atoms have been included in the structure factor calculations in calculated positions and have not been refined.

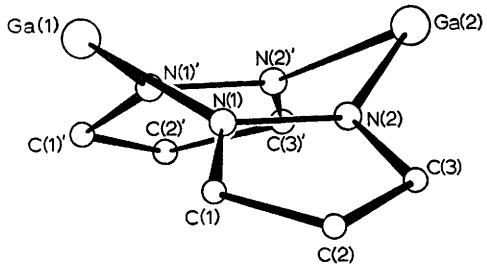

FIGURE. *Molecular structure of pyrazolyl-dideuteriogallane.*

The symmetrical six-membered Ga–(N–N–)$_2$Ga ring is in the boat conformation (which would also be predicted for the dimer in solution both on steric grounds and to account for the proton n.m.r. data), and lies on a crystallographic mirror plane (Figure). The mean Ga–N distance is 1·980(7) in good agreement with Ga–N distances in the previously documented gallane compounds, Me_3NGaH_3[7] and $[(CH_2)_2N{\cdot}GaH_2]_3$.[8] The mean dimensions for the remaining bond lengths are N–N 1·344(10), C–N 1·347(12), and C–C 1·355(16) Å, and for the bond angles N–Ga–N = 96·6(0·5), Ga–N–N = 123·5(0·6)°. The sum of the angles about each individual nitrogen atom equals 360° indicating a planar arrangement of bonds about these atoms. In addition the pyrazolyl rings themselves are planar ($\Sigma \angle$'s = 540°), the whole molecular arrangement thus allowing delocalization of 6π electrons in each C_3N_2 moiety, which presumably gives an added stability to the boat conformation. The deviation from a totally planar configuration for the whole tricyclic molecule, an arrangement which would also allow delocalization of the π-electrons but one which is somewhat more strained, is indicated by the angle between the plane formed by Ga(1), Ga(2), N(1), N(2), C(1), C(2), and C(3) and its corresponding mirror image. A planar arrangement would give this angle as 180°, the observed angle is 127·4°. The gallium atoms in fact lie 0·75 Ga(1) and 0·72 Ga(2) Å above the plane passing through the four nitrogen atoms. The Ga(1) · · · · · · · · Ga(2) and C(2) · · · · · · · C(2′) non-bonded intramolecular distances are 3·529(2) and 6·75(2) Å respectively.

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