

Synthesis and X-Ray Crystal Structure of the First Homoleptic Main Group Diazadiene Complex, Bis(1,4-di-*t*-butyl-1,4-diazabuta-1,3-diene)gallium

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Cocondensation of gallium vapour with 1,4-di-*t*-butyl-1,4-diazabuta-1,3-diene (Bu^tdab) affords the title compound as the first example of a homoleptic main group diazadiene complex; X-ray crystallography shows the molecule to possess distorted tetrahedral geometry, and together with e.s.r. and magnetic data suggests it to be a unique example of gallium(II) in which one of the diazadiene ligands has been doubly reduced.

Recently we described the metal atom synthesis of formally zero oxidation state homoleptic diazadiene complexes of titanium, yttrium, and some lanthanoid elements.¹ In this paper we report the synthesis and characterisation of the first homoleptic main group diazadiene complex.

Cocondensation of gallium vapour (generated from a resistively heated alumina crucible) with an excess of 1,4-di-*t*-butyl-1,4-diazabuta-1,3-diene (Bu^tdab) in toluene at 77 K yields a deep green-brown solution after warm-up to room temperature. Removal of the solvent and excess of Bu^tdab (by sublimation), followed by low temperature recrystallisation of the residue from toluene-hexane afforded green-black crystals of [Ga(σ,σ-N,N'-Bu^tdab)₂], (1) (satisfactory microanalyses have been obtained), in ca. 20% yield (4.0 g) based on gallium. The analogous indium compound could not be prepared using the same method.

Compound (1) is moderately soluble in hydrocarbon solvents and air-sensitive, thermally stable (m.p. 190–193 °C without decomposition, under argon), and may be sublimed at ca. 150 °C and 10⁻⁴ mbar with partial decomposition; a parent ion with the appropriate gallium isotope pattern was observed in the mass spectrum. Compound (1) is paramagnetic, with μ_{eff} = 1.7 μ_B at 308 K (Evans' method²), and its e.s.r. spectrum in hexane shows coupling to nitrogen and gallium at room temperature [Figure 1(a)]. Computer simulation [Figure 1(b)] based on the two magnetic isotopes of gallium (60% ⁶⁹Ga, 40% ⁷¹Ga, both *I* = 3/2) and four equivalent nitrogen atoms yields the following spin Hamiltonian parameters: *g*_{av.} = 2.00238, *A*_{av.}(Ga) = 18.39 × 10⁻⁴ cm⁻¹ and *A*_{av.}(N) = 2.638 × 10⁻⁴ cm⁻¹. The frozen solution spectrum at 130 K yields four gallium hyperfine resonances with nitrogen hyperfine coupling unresolved, possibly because of a more complex coupling pattern arising from coupling to two pairs of magnetically distinct nitrogen atoms, viz an anisotropic metal environment. This is consistent with the structure of (1) in the solid state, which has been established by single crystal X-ray diffraction, and is shown in Figure 2 together with significant bond distances and angles.[†]

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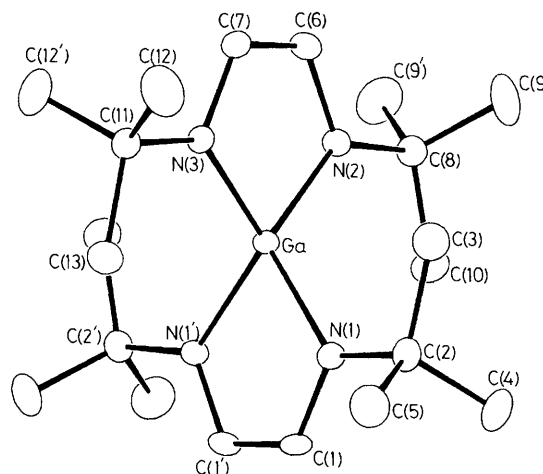


Figure 2. X-Ray crystal structure of (1). Selected bond lengths (Å): Ga–N(1), 1.864(4); Ga–N(2), 1.972(6); Ga–N(3), 1.966(5); N(1)–C(1), 1.395(6); N(2)–C(6), 1.331(9); N(3)–C(7), 1.321(9); C(1)–C(1'), 1.350(7); C(6)–C(7), 1.389(10). Selected angles (°): N(1)–Ga–N(1'), 90.4(2); N(2)–Ga–N(3), 84.9(2); N(1)–Ga–N(3), 121.3(2); N(1)–Ga–N(2), 121.3(1).

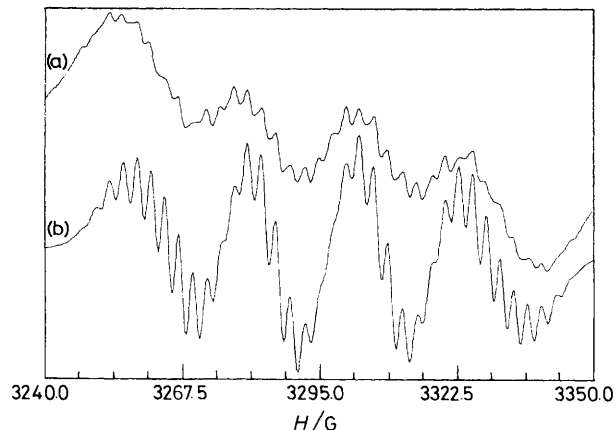


Figure 1. Experimental (a) and simulated (b) e.s.r. spectra of (1) (*G* = 10⁻⁴ T).

[†] Crystal data: C₂₀H₄₀GaN₄, *M* = 406.3, orthorhombic, space group *Pnmo*, *a* = 18.253(1), *b* = 13.522(1), *c* = 9.372(3) Å, *U* = 2313.2 Å³, *Z* = 4, *D*_c = 1.17 g cm⁻³, *F*(000) = 876. Monochromated Mo-*K*_α radiation, λ = 0.71069 Å, μ = 11.9 cm⁻¹. Data were collected on an Enraf-Nonius CAD4 diffractometer in the θ–2θ mode with Δθ = (0.8 + 0.35 tan θ)° and a maximum scan time of 1 min, using a crystal ca. 0.5 × 0.5 × 0.3 mm sealed in a capillary under argon. A total of 2335 unique reflections were measured for 2 < θ < 25° and +*h*, +*k*, +*l*, and 1356 reflections with |*F*²| > σ(*F*²) were used in the refinement where σ(*F*²) = [σ²(*I*) + (0.04)*I*]^{1/2}/*Lρ*. There was no crystal decay and no absorption corrections were applied.

The structure was solved by routine heavy atom methods and refined by full matrix least squares with nonhydrogen atoms anisotropic. Hydrogen atoms were located on a difference map and their positions refined but with their thermal parameters fixed at 1.3 × *B*_{equiv.} for the C atom to which they are bonded. The weighting scheme was ω = 1/σ²(*F*) and the final residuals were *R* = 0.040, *R*_w = 0.061. A final difference map was featureless. Programs from the Enraf-Nonius SDP-Plus package were run on a MicroVax computer. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

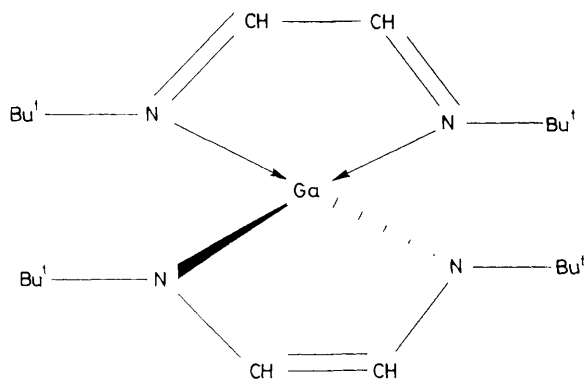


Figure 3. Bonding (1).

The molecule lies on a crystallographic mirror plane, the two planes defining the Bu^tdab ligands being mutually orthogonal, and exhibits distorted tetrahedral geometry around the central gallium atom. The average C=N and C-C bond lengths (1.326 and 1.389 Å respectively) in one of the Bu^tdab ligands in (1) are typical of those found in the transition metal analogues: for example [Mn(Bu^tdab)₂],⁴ in which the corresponding bond lengths are 1.32 and 1.38 Å. However, the values for the other Bu^tdab ligand show significant deviations: the C=N distance has lengthened to 1.395 Å, with a corresponding reduction in the C-C distance to 1.350 Å. These changes are accompanied by a decrease in

Ga-N distance from 1.969 to 1.864 Å, and an increase in the 'bite angle' of the ligand from 84.9 to 90.4°.

Consideration of these results suggests that one of the Bu^tdab ligands has been reduced to Bu^t-N⁻-CH=CH-N⁻-Bu^t, with concomitant oxidation of the metal centre to give a complex of, formally, gallium(II) as shown in Figure 3. This is confirmed by a magnetic moment which has the 'spin only' value for one unpaired electron, and an e.s.r. spectrum which shows coupling to both gallium and nitrogen. The reduction of the Bu^tdab ligand to give a metalladiazacyclopentene fragment may be compared with the extreme representation buta-1,3-diene-metal bonding as a metallacyclopentene.

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