X-Ray Structural Characterization of Bis[dimethylbis(1-pyrazolyl)-gallato]nickel(II)

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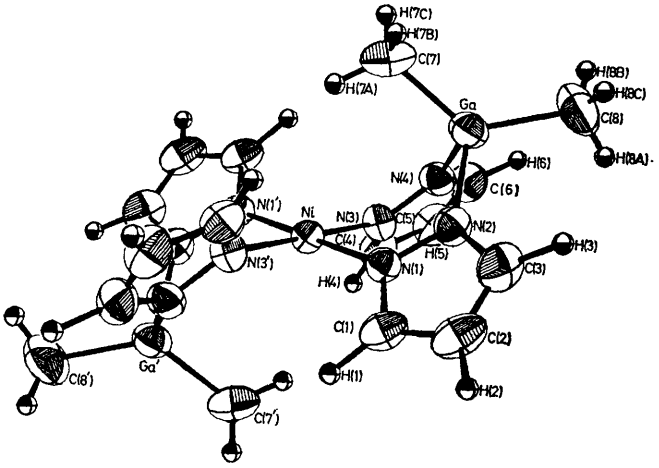
Summary The single crystal *X*-ray study of bis[dimethylbis(1-pyrazolyl)gallato]nickel(II) $[Me_2Ga(N_2C_3H_3)_2]_2Ni$, shows that the two six-membered $Ga(N-N)_2Ni$ rings are in the boat conformation with a planar arrangement of four nitrogen atoms about the nickel atom which lies on a crystallographic centre of symmetry, giving the whole molecule a pseudo chair conformation.

THE structural characterization of the symmetrical pyrazolyl dideuteriogallane dimer, $[N_2C_3H_3{\cdot}GaD_2]_2$ has been reported.[1] As part of a continuing investigation of pyrazolyl derivatives of aluminium and gallium[2] a number of chelating anionic ligands have now been synthesized.[3] The title complex was prepared from sodium dimethylbis(1-pyrazolyl)gallate and nickel chloride in aqueous solution. The complex was extracted with ether and recrystallized from xylene to yield air-stable, orange crystals suitable for *X*-ray study.

The crystals are monoclinic, $a = 8{\cdot}530$ (6), $b = 17{\cdot}939$ (10), $c = 7{\cdot}415$ (6) Å, $\beta = 106{\cdot}88$ (7)°, space group $P2_1/c$; $Z = 2$. A total of 1871 (1352 observed) independent reflections with $2\theta \leqslant 50°$ were measured on a Datex-automated G.E. XRD 6 diffractometer with Mo-K_α radiation ($\lambda = 0{\cdot}7107$ Å). The atomic positions were determined by Patterson and Fourier syntheses and refined by full-matrix least-squares methods with an empirical weighting scheme. The conventional R is 0·049 at the conclusion of refinement. The hydrogen atoms attached to the pyrazolyl rings were included in the refinement with isotropic thermal parameters but the methyl hydrogens proved difficult to locate in difference Fourier syntheses and were placed in calculated positions, allowed to contribute to the structure factor calculations, but not refined.

Crystal structures of a number of poly(1-pyrazolyl)-borate transition metal complexes have been summarized recently in the report on the structure of the tetrahedral cobalt complex, $[H_2B(N_2C_3H_3)_2]_2Co^{II}$,[4] but to date none of the group of square planar complexes has been structurally characterized, the square planar metal atom configuration being deduced from other physical measurements.[5] The present structure incorporating two gallium atoms clearly demonstrates the planar arrangement of four nitrogen atoms about the central nickel atom in this type of pyrazolyl complex, the nickel atom being located on a crystallographic centre of symmetry. The unsymmetrical $Ga(N-N)_2Ni$ six-membered rings are in the boat conformation with one boat above the nickel atom and one below it giving the whole molecule a pseudo chair conformation (Figure).



The mean Ga–N distance is 1·977 (4) Å in good agreement with previously documented gallane compounds Me_3NGaH_3,[6] $[(CH_2)_2NGaH_2]_3$[7] and $[N_2C_3H_3{\cdot}GaD_2]_2$.[1] The mean Ni–N distance of 1·895 (4) Å is also close to Ni–N distances previously reported for square planar NiN_4 systems.[8] The mean Ga–C distance is 1·944 (8) Å which is comparable to those Ga–C distances reported for the cyclic tetramer of dimethyl gallium hydroxide.[9] The mean dimensions for the remaining bond lengths are N–N 1·355 (4), C–N 1·333 (5), and C–C 1·377 (7) Å. Pertinent valency angles are N–Ga–N = 91·6 (0·2)°, Ga–N–N = 120·5 (0·3)° (mean), N–Ni–N (chelate angle) = 92·4 (0·2)°, N–Ni–N (non-chelate angle) = 87·6 (0·2)°, Ni–N–N = 124·0 (0·2)° (mean) and C(axial)–Ga–C(equatorial) = 126·9 (0·5)°. The sum of the angles

about each individual nitrogen atom equals 360° indicating a planar arrangement of the bonds about these atoms. In addition the pyrazolyl rings themselves are planar ($\Sigma\angle$'s = 540°). The angle between the planes formed by Ni, N(1), N(2), C(1), C(2), C(3), and Ga, and Ni, N(3), N(4), C(4), C(5), C(6), and Ga is 115·8° showing a larger deviation from a planar arrangement for the six-membered $Ga(N–N)_2Ni$ ring when compared to the corresponding angle of 127·4° for the dimer $[N_2C_3H_3{\cdot}GaD_2]_2$.[1] The angle between the square planar NiN_4 unit and the plane through C(7), C(8), Ga, Ni, Ga′, C(7)′ and C(8)′ is 94·1°.

The Ga · · · Ni non-bonded distance is 3·432 (1) Å and the Ni · · · C(axial) and Ni · · · C(equatorial) non-bonded distances are 3·553 (9) and 5·271 (9) Å respectively. The two Ni · · · C distances clearly demonstrate the non-equivalence of the methyl groups on the gallium atoms. Two axial methyl groups are positioned one above and one below the NiN_4 plane whilst the two equatorial methyl groups are positioned away from the nickel environment.

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[1] D. F. Rendle, A. Storr, and J. Trotter, *J.C.S. Chem. Comm.*, 1973, 189; *J.C.S. Dalton*, 1973, 2252.
[2] A. Arduini and A. Storr, *J.C.S. Dalton*, 1974, in the press.
[3] A. Storr and K. Breakell, unpublished results.
[4] L. J. Guggenberger, C. T. Prewitt, P. Meakin, S. Trofimenko, and J. P. Jesson, *Inorg. Chem.*, 1973, **12**, 508.
[5] J. P. Jesson, S. Trofimenko, and D. R. Eaton, *J. Amer. Chem. Soc.*, 1967, **89**, 3148.
[6] D. F. Shriver and C. E. Nordman, *Inorg. Chem.*, 1963, **2**, 1298.
[7] W. Harrison, A. Storr, and J. Trotter, *J.C.S. Dalton*, 1972, 1554.
[8] R. H. Holm and M. J. O'Connor, *Progr. Inorg. Chem.*, 1971, **14**, 241; N. F. Curtis, D. A. Swann, and T. N. Waters, *J.C.S. Dalton*, 1973, 1963.
[9] G. S. Smith and J. L. Hoard, *J. Amer. Chem. Soc.*, 1959, **81**, 3907.