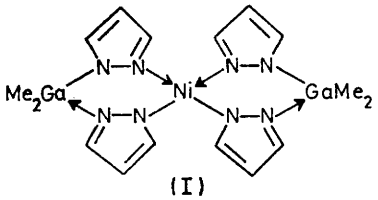
Crystal and Molecular Structure of Bis[dimethylbis(pyrazol-1-yl)gallato]-nickel(II) [1]

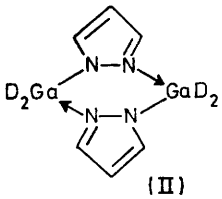
David F. Rendle, Alan Storr,* and James Trotter, Department of Chemistry, University of British Columbia, Vancouver, British Columbia, Canada V6T 1W5

Crystals of the title compound 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 $P2_1/c$, $Z = 2$. The structure was determined from diffractometer data by Patterson and Fourier syntheses, and refined by full-matrix least-squares methods to R 0·049 for 1352 observed reflexions. The whole molecule is in a pseudo-chair conformation with the two six-membered Ga–(N–N)$_2$–Ni rings in boat conformations. The nickel atom lies on a crystallographic centre of symmetry in the middle of a planar arrangement of four nitrogen atoms. Mean dimensions are: Ga–N 1·977, Ni–N 1·895, Ga–C 1·944, N–N 1·355, C–N 1·333, C–C 1·377 Å; N–Ga–N 91·6, Ga–N–N 120·5, C–Ga–C 126·9, N–Ni–N (chelate angle) 92·4, N–Ni–N (non-chelate angle) 87·6, Ni–N–N, 124°.

CRYSTAL structures of a number of poly(pyrazol-1-yl)-borate transition-metal complexes have been summarized recently in the report on the structure of the tetrahedral cobalt complex, $[Co^{II}\{H_2B(N_2C_3H_3)_2\}_2]$,[2] but none of the group of square-planar complexes, characterized by other physical measurements,[3] has been structurally investigated by X-ray methods. The present investigation involves the gallium complex (I), $[Ni^{II}\{Me_2Ga(N_2C_3H_3)_2\}_2]$,[1] and the results clearly



(I)



(II)

demonstrate a 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)$_2$–Ni six-membered rings are in the boat conformation with one boat above and the other below the nickel (see Figure 1) giving the whole molecule a pseudo-chair conformation. A similar boat conformation for the symmetrical six-membered Ga–(N–N)$_2$–Ga ring in the dideuterio(pyrazolyl)gallane dimer $[\{D_2Ga(N_2C_3H_3)\}_2]$ (II) has recently been demonstrated.[4]

EXPERIMENTAL

The title compound was prepared by mixing a 2 : 1 molar ratio of sodium dimethylbis(pyrazol-1-yl)gallate, $Na^+Me_2Ga(N_2C_3H_3)_2^-$, and nickel chloride in aqueous solution. The orange complex was extracted with diethyl ether and recrystallized from xylene as air-stable orange crystals suitable for X-ray study (Found: C, 36·6; H, 4·4; N, 21·4. $C_{16}H_{24}Ga_2N_8Ni$ requires C, 36·5; N, 21·3; H, 4·6%).

Crystal Data.—$C_{16}H_{24}Ga_2N_8Ni$, $M = 526{\cdot}1$, Monoclinic, $a = 8{\cdot}530(6)$, $b = 17{\cdot}939(10)$, $c = 7{\cdot}415(6)$ Å, $\beta = 106{\cdot}88(7)°$, $U = 1085{\cdot}7$ Å^3, $D_m = 1{\cdot}60$, $Z = 2$, $D_c = 1{\cdot}611$, $F(000) = 532$. Space group $P2_1/c$ (C_{2h}^5, No. 14) from systematic absences. Mo-K_α radiation, $\lambda = 0{\cdot}7107$ Å; μ(Mo-K_α) = 34·7 cm^{-1}.

The space group and initial unit-cell parameters were determined from oscillation, Weissenberg, and precession photographs. Accurate cell parameters were later obtained by a least-squares treatment of 23 $\sin^2\theta$ (hkl) values measured on a General Electric XRD 6 diffractometer with Mo-K_α radiation. Intensity data were collected on a Datex-automated General Electric XRD 6 diffractometer by the θ—2θ scan method at a rate of 2° min^{-1} in 2θ. The specimen used had dimensions *ca.* 0·3 × 0·02 × 0·7 mm^3 and was mounted with c^* parallel to the ϕ axis of the goniostat. A scintillation counter equipped with a zirconium filter and pulse-height analyser ensured approximately monochromatic radiation. Of the 1871 independent reflexions measured with $2\theta \leqslant 50°$, 1352 were considered observed, having $I > 3\sigma(I)$, where $\sigma^2(I) = S + B + (0{\cdot}5S)^2$ and S is the scan count, and B the background

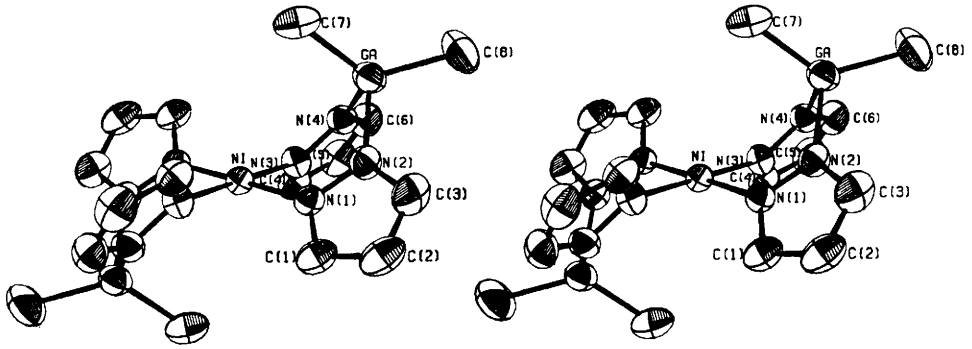


FIGURE 1 A stereoscopic view of the complex

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count. The intensity of a standard reflexion, monitored periodically, fluctuated by up to 11% throughout the data collection. The data were scaled and the structure amplitudes derived by the usual methods. No absorption corrections were applied.

The co-ordinates of the gallium atom were deduced from a three-dimensional Patterson function, those of the nickel atom being already fixed at 0,0,0. A Fourier synthesis phased on these two atoms revealed the remainder of the non-hydrogen atom positions, and two cycles of full-matrix least-squares refinement with isotropic temperature factors for all atoms resulted in R 0·080. The function minimized in the refinement was $\Sigma w(F_o - F_c)^2$ with $\sqrt{w} = F_o/12{\cdot}0$ when $F_o \leqslant 12{\cdot}0$, $\sqrt{w} = 19{\cdot}0/F_o$ when $F_o \geqslant 19{\cdot}0$, and $\sqrt{w} = 1$ when $12{\cdot}0 < F_o < 19{\cdot}0$. A difference-Fourier synthesis revealed the positions of the hydrogen atoms attached to the pyrazolyl rings, but the methyl hydrogen atoms could not be located with any certainty. At this stage six reflexions (004, 013, 020, 021, 042, and −191) considered to suffer from extinction effects were given zero weight in the refinement. Convergence was reached after two cycles of full-matrix least-squares refinement in which all non-hydrogen atoms were refined with anisotropic thermal parameters and the pyrazolyl hydrogen atoms were refined with isotropic thermal parameters.

TABLE 1

Final positional (fractional $\times 10^5$ for Ga, $\times 10^4$ for others) parameters, with estimated standard deviations in parentheses

	x	y	z
Ga	29787(9)	−11568(5)	26780(12)
Ni	0	0	0
N(1)	−437(7)	−1008(3)	478(7)
N(2)	669(7)	−1465(3)	1633(8)
N(3)	1050(7)	187(3)	2578(8)
N(4)	2329(7)	−217(3)	3654(3)
C(1)	−1878(10)	−1365(4)	−136(11)
C(2)	−1706(11)	−2072(5)	649(13)
C(3)	−96(11)	−2110(4)	1740(13)
C(4)	762(11)	741(4)	3616(11)
C(5)	1844(12)	692(5)	5414(12)
C(6)	2789(11)	90(5)	5355(10)
C(7)	3779(11)	−937(6)	542(14)
C(8)	4014(14)	−1798(6)	4817(17)
H(1)	−2944(135)	−980(58)	−942(142)
H(2)	−2757(143)	−2441(56)	140(146)
H(3)	621(119)	−2544(55)	2660(129)
H(4)	−125(90)	1008(38)	3296(88)
H(5)	1772(119)	954(54)	6172(136)
H(6)	3722(144)	−102(60)	6702(154)
H(7A)	3002	−599	−399
H(7B)	3936	−1404	−144
H(7C)	4885	−671	957
H(8A)	3311	−1828	5704
H(8B)	5115	−1594	5542
H(8C)	4164	−2316	4383

The methyl hydrogen atoms were placed in calculated positions (with B_{iso} 5·0 Å^2) assuming ideal sp^3 geometry at the relevant carbon atoms and C–H 1·0 Å. Their parameters were not refined. The final conventional R is 0·049 and the weighted residual R' [defined as $\Sigma w(F_o - F_c)^2/\Sigma w F_o^2$] is 0·068 for the observed reflexions. The maximum shift-to-error ratio in the refined parameters was 0·78. The choice of weighting scheme appeared to be justified as an approximately constant value for $w\Delta^2$ was observed over the ranges of F_o considered. The error in an observation of unit weight was 1·17. A final difference-Fourier synthesis showed fluctuations of ±0·63 eÅ^{-3}.

Scattering factors for gallium, nickel, nitrogen, and carbon were taken from ref. 5 and those for hydrogen were from ref. 6. Those for gallium and nickel were corrected for the effects of the real and imaginary parts of anomalous dispersion (ref. 7). Measured and calculated structure amplitudes are listed in Supplementary Publication No. SUP 21148 (18 pp., 1 microfiche)*. Final positional and thermal parameters are given in Tables 1 and 2.

TABLE 2

Final thermal parameters,* with estimated standard deviations in parentheses

(*a*) Anisotropic thermal parameters, $10^3\ U_{ij}$/Å^2

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ga	42(1)	48(1)	57(1)	5(1)	12(1)	3(1)
Ni	36(1)	34(1)	34(1)	−3(1)	10(1)	−2(1)
N(1)	37(3)	36(3)	38(3)	−3(2)	10(2)	−1(2)
N(2)	49(3)	37(3)	51(3)	−4(3)	13(3)	2(3)
N(3)	47(3)	39(3)	40(3)	1(2)	9(3)	−1(2)
N(4)	39(3)	53(3)	41(3)	−1(3)	7(2)	−3(3)
C(1)	51(4)	48(4)	56(5)	−15(3)	22(4)	−13(3)
C(2)	64(5)	57(5)	74(5)	−30(4)	29(4)	−16(4)
C(3)	73(6)	32(4)	78(6)	−10(4)	26(5)	−3(3)
C(4)	59(5)	49(4)	49(4)	−2(4)	24(4)	−8(3)
C(5)	78(6)	61(5)	42(5)	−10(4)	20(4)	−18(4)
C(6)	56(5)	77(6)	35(4)	−14(4)	3(3)	−4(4)
C(7)	54(5)	77(6)	83(6)	−3(4)	35(4)	−14(5)
C(8)	72(6)	85(7)	99(7)	22(6)	4(6)	33(6)

(*b*) Isotropic thermal parameters, Å^2 × 10^2

Atom	U_{iso}	Atom	U_{iso}
H(1)	8(3)	H(4)	3(1)
H(2)	9(3)	H(5)	5(2)
H(3)	8(2)	H(6)	8(3)

* In the form: $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

DISCUSSION

The present structural analysis clearly confirms the square-planar arrangement of the four chelating nitrogen atoms about the central nickel atom in this pyrazolylgallate complex. A stereoscopic view of the molecule is shown in Figure 1. Individual distances and angles are listed in Table 3 and selected least-squares planes and dihedral angles are given in Table 4. The Ga···Ni intramolecular distance of 3·432 Å is close to the Ga···Ga distance in (II).[4] The Ni···C(ax) and Ni···C(eq) non-bonded intramolecular distances (3·553 and 5·271 Å) clearly demonstrate the blocking of potential octahedral co-ordination sites above and below the NiN_4 plane by the two axial methyl groups (see Figure 1) and also the pronounced boat conformation of the Ga–$(N–N)_2$–Ni six-membered rings. The mean Ga–N distance [1·977 (4) Å] agrees well with the corresponding distances previously reported for compounds containing tetrahedrally co-ordinated gallium atoms *viz.* $[Me_3NGaH_3]$ [1·97(9) Å],[8] $[\{(CH_2)_2NGaH_2\}_3]$ [1·97 (2) Å],[9] and in (II) [1·974 (7) Å].[4] The mean Ni–N distance

* For details see notice to authors No. 7, in *J.C.S. Dalton*, 1973, Index issue.

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[1·895 (4) Å] is also close to previously reported values for square planar NiN_4 systems,[10,11] and the mean Ga–C distance [1·944 (8) Å] is comparable to those reported for the cyclic tetramer [$\{Me_2GaOH\}_4$].[12] Mean

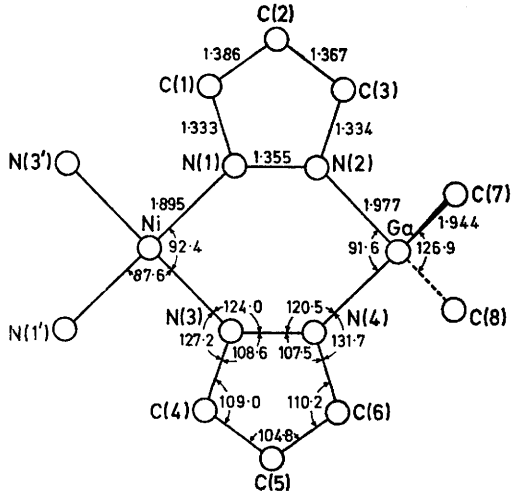

FIGURE 2 Mean dimensions for the [$\{Me_2Ga(N_2C_3H_3)_2\}_2Ni$] complex

TABLE 3

Bond lengths (Å), and valency angles (°), with standard deviations in parentheses

(*a*) Bond distances

Ga–N(2)	1·976(6)	C(2)–C(3)	1·378(13)
Ga–N(4)	1·977(6)	C(4)–C(5)	1·387(12)
Ga–C(7)	1·938(9)	C(5)–C(6)	1·356(13)
Ga–C(8)	1·950(10)	C(1)–H(1)	1·16(11)
Ni–N(1)	1·899(5)	C(2)–H(2)	1·09(11)
Ni–N(3)	1·891(5)	C(3)–H(3)	1·10(10)
N(1)–N(2)	1·352(8)	C(4)–H(4)	0·87(8)
N(3)–N(4)	1·359(8)	C(5)–H(5)	0·75(10)
N(1)–C(1)	1·343(9)	C(6)–H(6)	1·14(11)
N(2)–C(3)	1·341(10)		
N(3)–C(4)	1·322(9)		
N(4)–C(6)	1·327(9)		
C(1)–C(2)	1·385(12)		

(*b*) Valency angles

N(2)–Ga–N(4)	91·6(0·2)	N(1)–Ni–N(3)	92·4(0·2)
N(2)–Ga–C(7)	106·5(0·3)	N(1')–Ni–N(3)	87·6(0·2)
N(2)–Ga–C(8)	108·6(0·4)	Ni–N(1)–N(2)	123·9(0·4)
N(4)–Ga–C(7)	109·2(0·3)	Ni–N(1)–C(1)	126·9(0·5)
N(4)–Ga–C(8)	108·3(0·4)	C(1)–N(1)–N(2)	109·0(0·6)
C(7)–Ga–C(8)	126·9(0·5)	N(1)–N(2)–Ga	120·7(0·4)
N(1)–N(2)–C(3)	107·4(0·6)	C(5)–C(6)–N(4)	110·3(0·7)
Ga–N(2)–C(3)	131·7(0·6)	N(1)–C(1)–H(1)	113·2(5·5)
Ni–N(3)–N(4)	124·2(0·4)	C(2)–C(1)–H(1)	137·1(5·6)
Ni–N(3)–C(4)	127·5(0·5)	C(1)–C(2)–H(2)	115·7(5·5)
C(4)–N(3)–N(4)	108·2(0·6)	C(3)–C(2)–H(2)	138·8(5·6)
Ga–N(4)–N(3)	120·2(0·4)	C(2)–C(3)–H(3)	132·9(5·4)
Ga–N(4)–C(6)	131·7(0·6)	N(2)–C(3)–H(3)	117·1(5·4)
N(3)–N(4)–C(6)	107·6(0·6)	N(3)–C(4)–H(4)	123·3(4·3)
N(1)–C(1)–C(2)	108·7(0·7)	C(5)–C(4)–H(4)	125·5(4·3)
C(1)–C(2)–C(3)	104·9(0·8)	C(4)–C(5)–H(5)	120·3(7·7)
C(2)–C(3)–N(2)	110·0(0·7)	C(6)–C(5)–H(5)	134·8(7·7)
N(3)–C(4)–C(5)	109·2(0·8)	C(5)–C(6)–H(6)	119·0(5·7)
C(4)–C(5)–C(6)	104·7(0·8)	N(4)–C(6)–H(6)	130·5(5·7)

bond lengths and angles within the pyrazolyl moieties are, as expected, very similar to those in the dideuteriogallane dimer (II),[4] and in similar pyrazolylborate complexes.[2] The planarity of the pyrazolyl rings (sum of angles 540°) is reflected in the best least-squares planes through the ring atoms (Table 4). The angle (116·4°) between planes (2) and (4) shows a larger deviation from planarity than was observed in (II).[4] The angle between the square-planar NiN_4 unit [plane (5)] and that through the atoms C(7), C(8), Ga, and Ni [plane (8)] is 94·1°. The relevant details of the overall stepped structure [10] (Figure 1) are given by the perpendicular distance of 1·65 Å between the mean planes through the atoms N(1)—(4) and through the atoms N(1')—(4'), and by the dihedral angle of 39·0° between the mean planes through the atoms N(1)—(4) and through the atoms Ni, N(1), and N(3). Molecular geometry calculations revealed no important intermolecular non-bonded interactions <3·5 Å.

TABLE 4

(*a*) Equations of weighted best planes in the form $lX + mY + nZ = p$ where X, Y, Z are orthogonal co-ordinates in Å. Deviations (Å) of atoms from the planes are given in square brackets

Plane (1): N(1), N(2), C(1)—(3)

$0{\cdot}5130X - 0{\cdot}3510Y - 0{\cdot}7833Z = -0{\cdot}1267$

[Ga −0·121(1), Ni 0·125(1), N(1) 0·001(5), N(2) −0·001(6), C(1) −0·002(8), C(2) 0·002(9), C(3) 0·000(9)]

Plane (2): Ga, Ni, N(1), N(2), C(1)—(3)

$0{\cdot}4764X - 0{\cdot}3049Y - 0{\cdot}8246Z = -0{\cdot}0009$

[Ga −0·001(1), Ni 0·001(1), N(1) −0·044(5), N(2) 0·051(6), C(1) −0·076(8), C(2) 0·008(9), C(3) 0·083(9)]

Plane (3): N(3), N(4), C(4)—(6)

$0{\cdot}7585X + 0{\cdot}5845Y - 0{\cdot}2881Z = 0{\cdot}0677$

[Ga 0·203(1), Ni −0·068(1), N(3) 0·005(6), N(4) −0·004(6), C(4) −0·008(9), C(5) 0·005(10), C(6) 0·002(9)]

Plane (4): Ga, Ni, N(3), N(4), C(4)—(6)

$0{\cdot}8093X + 0{\cdot}5242Y - 0{\cdot}2650Z = 0{\cdot}0007$

[Ga 0·001(1), Ni −0·001(1), N(3) 0·032(6), N(4) −0·081(6), C(4) 0·086(9), C(5) 0·037(10), C(6) −0·071(9)]

Plane (5): Ni, N(1), N(3)

$0{\cdot}9532X - 0{\cdot}2744Y - 0{\cdot}1271Z = 0{\cdot}0000$

Plane (6): N(1)—(4)

$0{\cdot}7636X + 0{\cdot}1131Y - 0{\cdot}6357Z = 0{\cdot}8208$

[Ga −0·878(1), Ni −0·821(1), N(1) −0·038(6), N(2) 0·046(6), N(3) 0·044(6), N(4) −0·045(6)]

Plane (7): Ga, N(2), N(4)

$0{\cdot}2222X + 0{\cdot}4549Y - 0{\cdot}8624Z = 2{\cdot}1463$

Plane (8): Ga, Ni, C(7), C(8)

$-0{\cdot}3672X - 0{\cdot}7928Y - 0{\cdot}4864Z = 0{\cdot}0000$

[Ga 0·000(1), Ni 0·0, C(7) −0·005(10), C(8) −0·018(12)]

(*b*) Dihedral angles (°) between planes

(1)–(2)	4·1	(2)–(4)	116·4
(3)–(4)	4·7	(5)–(8)	94·1
(5)–(6)	39·0		

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