Synthesis of Pyrazolyl-borate, -aluminate, -gallate, and -indate Ligands, and their Chelating Properties towards Cobalt(II), Nickel(II), Copper(II), and Zinc(II)

By **Kenneth R. Breakell** (in part), **David J. Patmore**, and **Alan Storr**,* Department of Chemistry, University of British Columbia, Vancouver, Canada V6T 1W5

The uninegative dimethylbis(pyrazol-1-yl)- and bis(3,5-dimethylpyrazol-1-yl)dimethyl-gallate ions have been isolated as their sodium and tetra-alkylammonium salts. The anions act as bidentate chelating agents towards transition-metal ions. The orange air-stable nickel complex $[Ni\{Me_2Ga(pz)_2\}_2]$ (pz = pyrazolyl) has a square-planar arrangement of four nitrogens about the nickel atom, while the purple oxygen-sensitive cobalt complex $[Co\{Me_2Ga(pz)_2\}_2]$ exhibits the transition metal in a tetrahedral environment. Steric requirements of the two ligands are emphasised in the two copper complexes $[Cu\{Me_2Ga(pz)_2\}_2]$ and $[Cu\{Me_2Ga(dmpz)_2\}_2]$ (dmpz = 3,5-dimethylpyrazolyl) which, respectively, display the copper atoms in square-planar and pseudo-tetrahedral environments. The $[Me_2B(pz)_2]^-$ ligand has been synthesized and utilized to prepare nickel(II), copper(II), and zinc(II) complexes for comparative purposes. Representative pyrazolyl-aluminate and -indate ligands have also been synthesized, but attempts to complex these with transition-metal ions have so far proved unsuccessful.

NUMEROUS transition-metal complexes incorporating pyrazolylborate ligands have been studied in recent years,[1-4] but to date complexes involving pyrazolyl derivatives of the heavier Group 3 elements as ligands have not been reported with the exception of a preliminary crystal-structure study.[5] As part of a general investigation into pyrazolyl (pz) derivatives of aluminium and gallium,[6,7] anionic chelating ligands have been synthesized and a number of their transition-metal complexes studied. The observed air stability of the dimethylgallium moiety in the dimer $[\{Me_2Ga(pz)\}_2]$ [6] prompted the synthesis of the sodium dimethylbis(pyrazol-1-yl)gallate salt. The route in equations (1)—(3) was employed.

$$NaH + N_2C_3H_4 \xrightarrow[N_2]{thf} Na(N_2C_3H_3) + H_2 \qquad (1)$$

$$Na(N_2C_3H_3) + Me_3Ga \xrightarrow[N_2]{thf} Na[Me_3Ga(N_2C_3H_3)] \qquad (2)$$

$$Na[Me_3Ga(N_2C_3H_3)] + N_2C_3H_4 \xrightarrow[N_2,\ reflux]{thf} Na[Me_2Ga(N_2C_3H_3)_2] + CH_4 \qquad (3)$$

After removal of solvent the product was isolated as a slightly hygroscopic white solid, incorporating, as expected, an air-stable ' Me_2Ga ' moiety. Use of excess of pyrazole in step (3) did not cause further substitution at the gallium atom and the sodium dimethylbis(pyrazol-1-yl)gallate salt remained as the only product after removal of volatiles. Ligands containing other Group 3 elements were prepared by similar routes, but it was noted that with aluminium trialkyls excess of pyrazole in step (3) caused loss of all alkyl groups from the aluminium atom and formation of the tetrakis(pyrazol-1-yl)aluminate ion, $[Al(pz)_4]^-$. Transition-metal complexes of the two gallium ligands and the $[Me_2B(pz)_2]^-$ ligand were prepared by the reaction of suitable transition-metal salts and the ligands in thf (tetrahydrofuran) as solvent, followed by extraction and recrystallization procedures. Analytical results for the ligands and for the complexes isolated are collected in Table 1, ^1H n.m.r. data in Table 2, and electronic absorption spectra and magnetic measurements in Table 3.

TABLE 1

Analytical data (%) for ligand salts and complexes

Complex	Colour	Found				Calc.			
		C	H	N	Other	C	H	N	Other
$Na[Me_2Ga(pz)_2]$	White	37·3	4·7	21·7	Ga 26·8	37·4	4·7	21·8	Ga 27·1
$[Me_4N][Me_2Ga(pz)_2]$	White	46·5	8·8	22·4		46·2	9·0	22·4	
$[Et_4N][Me_2Ga(dmpz)_2]$	White	56·0	8·8	16·0		57·2	9·5	16·7	
$[Et_4N][Me_2In(pz)_2]$	White	46·4	8·5	16·4		46·9	7·8	17·1	
$Na[Al(pz)_4]$	White				Al 8·6				Al 8·5
$Na[H_2Ga(pz)_2]$	White				Ga : H = 1 : 1·90				Ga : H = 1 : 2
$[Ni\{Me_2Ga(pz)_2\}_2]$	Orange	36·6	4·4	21·4		36·5	4·6	21·3	
$[Cu\{Me_2Ga(pz)_2\}_2]$	Lilac	36·2	4·7	21·1		36·2	4·5	21·1	
$[Co\{Me_2Ga(pz)_2\}_2]$	Purple	34·8	3·7	21·5		36·5	4·6	21·3	
$[Cu\{Me_2Ga(dmpz)_2\}_2]$	Red	44·8	6·3	17·6		44·8	6·2	17·4	
$[Co\{Me_2Ga(dmpz)_2\}_2]$	Purple	43·2	5·8	17·1		45·1	6·3	17·5	
$[Ni\{Me_2B(pz)_2\}_2]$	Orange	47·1	6·1	27·7		47·0	5·9	27·4	
$[Cu\{Me_2B(pz)_2\}_2]$	Lilac	46·4	5·7	27·2		46·5	5·8	27·1	
$[Zn\{Me_2B(pz)_2\}_2]$	White	46·2	5·6	27·2		46·3	5·8	27·0	

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[1] S. Trofimenko, *Chem. Rev.*, 1972, **72**, 497.

[2] R. B. King and A. Bond, *J. Amer. Chem. Soc.*, 1974, **96**, 1334, 1338, 1343.

[3] F. A. Cotton, B. A. Frenz, and A. G. Stanislowski, *Inorg. Chim. Acta*, 1973, **7**, 503.

[4] F. A. Cotton, T. LaCour, and A. G. Stanislowski, *J. Amer. Chem. Soc.*, 1974, **96**, 754.

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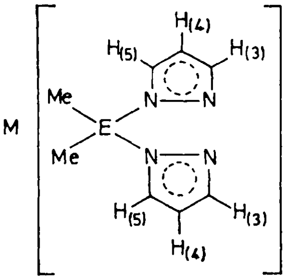
[6] A. Arduini and A. Storr, *J.C.S. Dalton*, 1974, 503.

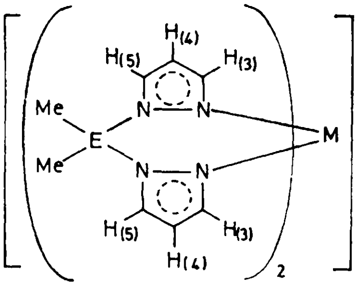
[7] D. F. Rendle, A. Storr, and J. Trotter, *J.C.S. Dalton*, 1973, 2252.

TABLE 2

^1H N.m.r. data[a]



E	M	τ_{E-Me}	$\tau_{H(5)}$	$\tau_{H(3)}$	$\tau_{H(4)}$	Others
B	Na[b]	9·7 (s)	2·50 (dd)[c]	2·72 (dd)[d]	4·10 (t)[e]	
Ga	Me_4N[b]	10·26 (s)	2·50 (d)[f]		3·95 (t)[g]	τ_{N-Me} 6·84
In	Na[b]	10·32 (s)	2·52 (br)		3·91 (br)	
In	Et_4N[b]	10·20 (s)	2·53 (d)[h]		3·97 (t)[h]	τ_{N-Et} 8·87 (m), 6·15 (q)
$Na[Me_2Ga(dmpz)_2]$		10·45 (s)			4·24 (s)	τ_{Me_2-pz} 7·90 (s)



E	M	τ_{E-Me}	$\tau_{H(5)}$	$\tau_{H(3)}$	$\tau_{H(4)}$	Others
B	Zn	9·49 (s)	2·53 (dd)[c]	2·24 (dd)[i]	3·80 (t)[j]	
B	Ni	9·43 (s), 7·84 (s)	2·50 (dd)[c]	3·24 (dd)[i]	4·00 (t)[j]	
Ga	Ni	9·69 (s), 8·29 (s)	2·53 (d)[j]	3·21 (d)[j]	4·01 (t)[j]	
Ga	Cu					7·5 (vbr), 8·7 (w), 9·0 (w)
$[Cu\{Me_2Ga(dmpz)_2\}_2]$		9·49 (br)				τ_{Me_2-pz} 5·6 (br)

s = Singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quartet, m = multiplet, br = broad, w = weak, and vbr = very broad.

[a] All spectra were measured in $CDCl_3$ unless otherwise noted. [b] Spectra measured in $(CD_3)_2CO$. [c] $J[H_{(4)}H_{(5)}]$ 2·2, $J[H_{(3)}H_{(5)}]$ 0·6 Hz. [d] $J[H_{(3)}H_{(4)}]$ 1·8, J[H(3)H(5)] 0·6 Hz. [e] J 1·8 Hz. [f] J 1·2 Hz. [g] J 1·6 Hz. [h] J 1·7 Hz. [i] J[H(3)H(4)] 2·2, J [H(3)H(5)] 0·6 Hz. [j] J 2·2 Hz.

TABLE 3

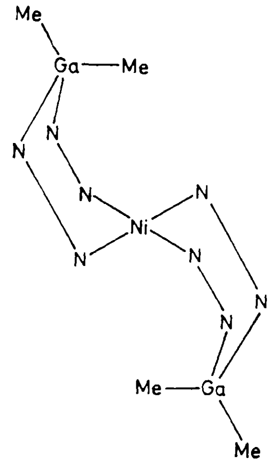
Electronic absorption spectra ($\nu_{max.}$/cm^{-1}) and magnetic moments of pyrazolyl-gallate and -borate transition-metal complexes

Complex	Solution spectra[a]		Reflectance spectra[b]	μ[c]/B.M.
$[Ni\{Me_2Ga(pz)_2\}_2]$	36 760	(2 150)	21 740	0
	22 120	(68)		
$[Ni\{Me_2B(pz)_2\}_2]$	37 310	(1 790)	20 800	0
	21 370	(65)		
$[Cu\{Me_2Ga(pz)_2\}_2]$	29 580	(1 185)		
	15 380	(93)	19 800	1·84
	12 500 (sh)	(66)	16 950	
$[Cu\{Me_2B(pz)_2\}_2]$	31 640	(1 140)		
	20 000	(33)	19 420	1·82
	16 950 (sh)	(25)	17 090	
$[Cu\{Me_2Ga(dmpz)_2\}_2]$	37 730	(2 790)		
	24 690	(1 900)	25 000	
	20 200	(1 970)	19 610	1·87
	11 980 (sh)	(71)		
	9 380	(160)		
$[Co\{Me_2Ga(pz)_2\}_2]$[d]	19 460	(443)		
	18 050	(594)		
	16 580	(456)		4·8
	9 090	(155)		
	8 470	(146)		

[a] Measured in cyclohexane solution; ε values (l mol^{-1} cm^{-1}) are given in parentheses. [b] Measured between 13 500 and 28 600 cm^{-1} using powdered samples. [c] Corrected for ligand and metal diamagnetism. [d] Electronic spectrum measured in benzene solution.

RESULTS AND DISCUSSION

Nickel Complexes.—Two square-planar nickel complexes were characterized and both exhibit zero magnetic moments as predicted for square-planar d^8 nickel systems. The crystal structure [5] of the [Ni{$Me_2Ga(pz)_2$}$_2$] complex clearly demonstrates the square-planar environment of the nickel atom located at the centre of the plane of the four co-ordinated nitrogen atoms. The structure confirms the predicted boat conformations for the six-membered Ga–(N–N)$_2$–Ni rings, one ring positioning a gallium atom above the NiN_4 plane, the other ring positioning the second gallium atom below this plane (see Figure). The boat conformations allow, on the one hand, a planarity about the nitrogen atoms and a planarity for the pz moieties with consequent gain in stabilization resulting from a delocalization of 6 π-electrons in each of the five-membered organic heterocyclic moieties, and, on the other hand, a less angularly strained environment for the four-co-ordinate gallium atoms at the bow-spit positions. The structure gives two unique environments for the Ga–*Me* groups, and the differently located methyl groups were clearly distinguishable in the ^1H n.m.r. spectrum of the complex in solution (Table 2) at room temperature. One Ga–*Me* signal, at τ 9·69, occurred at a position close to the signals observed for Ga–*Me* groups in non-transition-metal derivatives [6,8] and is assigned to the methyl groups positioned away from the nickel environment and in pseudo-equatorial positions on the gallium atoms. The second Ga–*Me* signal occurs at much lower field than usual (τ 8·29) and is assigned to the methyl groups pseudo-axial on the gallium atoms, which occupy positions in close proximity to the nickel atom above and below the NiN_4 plane, effectively blocking these as potential octahedral co-ordination sites. A similar spectrum was observed for the boron analogue [Ni{$Me_2B(pz)_2$}$_2$] (see Table 2) and also by Trofimenko [9] for the [Ni{$R_2B(pz)_2$}$_2$] (where R = Et or Bu^n) complexes. Stereochemical non-rigidity for both [Ni{$Me_2Ga(pz)_2$}$_2$] and [Ni{$Me_2B(pz)_2$}$_2$] in solution has been demonstrated by a variable-temperature ^1H n.m.r. study.[10]



Proposed 'frozen' molecular arrangement for [Ni{$Me_2Ga(pz)_2$}$_2$] (C_3H_3 moieties of pz rings have been omitted for clarity)

The mass spectrum of [Ni{$Me_2Ga(pz)_2$}$_2$] did not display a parent-ion cluster but did give its strongest peaks corresponding to loss of one and two methyl groups from the parent ion, thus confirming a similar molecular constitution in the gas phase as in the solid and in solution for the complex. (A similar absence of parent ions in the mass spectra of organo-gallium and -aluminium compounds has been reported previously.[6,11,12]) The most intense peaks in the present spectrum, corresponding to fragments containing two gallium and one nickel atoms, occurred as characteristic quartets with individual peaks at separations of two mass units (*e.g.* [Ni{$Me_3Ga_2(pz)_4$}]$^+$ 509—515, [Ni{$Me_2Ga_2(pz)_4$}]$^+$ 494—500), the relative abundances of which agree well with those predicted from isotopic abundances of the metal atoms (^{69}Ga 60, ^{71}Ga 40, ^{58}Ni 70, and ^{60}Ni 26%). Similarly, for fragments containing one gallium atom and one nickel atom, triplets were observed (*e.g.* [Ni{$MeGa(pz)_3$}]$^+$ 343—347, the third most intense signal in the spectrum), and for fragments containing one metal atom doublets were observed (*e.g.* [MeGa(pz)]$^+$ 151—153).

Electronic spectra (see Table 3) of both the [Ni{$Me_2Ga(pz)_2$}$_2$] and [Ni{$Me_2B(pz)_2$}$_2$] complexes are consistent with a square-planar environment for the nickel atom. In each case one absorption band, attributable to a *d*–*d* transition ($^1A_{1g} \rightarrow {}^1A_{2g}$) of the square-planar d^8 system, was observed. The position of the band and the absorption coefficient for the boron complex agree closely with the values reported by Jesson *et al.*[13] for the similar boron complex, [Ni{$H_2B(pz)_2$}$_2$].

Our inability to prepare [Ni{$Me_2Ga(dmpz)_2$}$_2$] (dmpz = 3,5-dimethylpyrazol-1-yl) suggests that either the ligand itself is unstable under the reaction conditions, or that the adoption of a pseudo-tetrahedral arrangement of nitrogen atoms about the nickel atom, to remove the steric interactions inherent in a square-planar system, is for some reason not possible. This behaviour is to be contrasted with the proven stability of the corresponding pseudo-tetrahedral copper complex, [Cu{$Me_2Ga(dmpz)_2$}$_2$] (see below).

Copper Complexes.—Three copper complexes were characterized and constitute part of a detailed spectroscopic study.[10] The [Cu{$Me_2Ga(pz)_2$}$_2$] and [Cu{$Me_2B(pz)_2$}$_2$] complexes display the copper atom in a square-planar environment of the four chelating nitrogen atoms. The gallium complex is isomorphous with its nickel analogue and has been characterized by

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[8] A. Storr and B. S. Thomas, *J. Chem. Soc.* (*A*), 1971, 3850.

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[10] F. G. Herring, D. J. Patmore, and A. Storr, *J.C.S. Dalton*, 1975, 711.

[11] B. D. Chambers, G. E. Coates, F. Glockling, and M. Weston, *J. Chem. Soc.* (*A*), 1969, 1712.

[12] K. J. Alford, K. Gosling, and J. D. Smith, *J.C.S. Dalton*, 1972, 2203.

[13] J. P. Jesson, S. Trofimenko, and D. R. Eaton, *J. Amer. Chem. Soc.*, 1967, **89**, 3148.

X-ray structural analysis.[14] The third complex, [Cu-{$Me_2Ga(dmpz)_2\}_2$] displays the copper atom in a pseudo-tetrahedral environment. From a molecular-model study, steric interactions, inherent in a square-planar system incorporating the 3,5-dimethylpyrazol-1-yl moiety in the ligands, are minimized in the tetrahedral situation, particularly if the six-membered Ga–(N–N)$_2$–Cu rings are planar rather than in boat conformations. *X*-Ray structural analysis has shown this to be so in the solid state with almost planar Cu–(N–N)$_2$–Ga rings and the three heavy atoms on a two-fold axis.[14] The angle between the chelating CuN_2 fragments is 72°.

The magnetic moments of the three copper complexes are as predicted for d^9 Cu^{II} systems. The e.s.r. spectra of the complexes clearly distinguish between the two square-planar complexes on the one hand and the tetrahedral complex on the other.[10]

Cobalt Complexes.—The cobalt complex, [Co{$Me_2Ga(pz)_2\}_2$], is a very oxygen-sensitive material, changing rapidly from purple to a puce colour on exposure to oxygen. It is very soluble in organic solvents and defied attempts at recrystallization. The magnetic moment of 4·8 B.M.,* and the electronic-absorption spectrum consisting of two bands attributable to the $^4A_2 \rightarrow {}^4T_1(F)$ ($\nu_{max.}$ at 8 470 and 9 090 cm^{-1}) and $^4A_2 \rightarrow {}^4T_1(P)$ ($\nu_{max.}$ at 16 580, 18 050, and 19 460 cm^{-1}) transitions, both suggest a tetrahedral environment for the cobalt atom. The results are comparable to those reported by Jesson *et al.*[13] for the similar tetrahedral cobalt complex [Co{$H_2B(pz)_2\}_2$], which has also recently been characterized by *X*-ray structural analysis.[15] Large splittings observed in the $^4A_2 \rightarrow {}^4T_1(F)$ and $^4A_2 \rightarrow {}^4T_1(P)$ transitions may be attributed to the effect of spin–orbit coupling and low-symmetry components in the crystal field. The $^4A_2 \rightarrow {}^4T_2(F)$ transition was not characterized and probably lies in the i.r. region of the spectrum. A notable distinction between the [Co{$Me_2Ga(pz)_2\}_2$] and [Co{$H_2B(pz)_2\}_2$] complexes lies in their stability towards oxygen. The gallium complex is extremely oxygen sensitive whereas the boron complex is quite stable. A possible explanation is that the M–(N–N)$_2$–Co (M = B or Ga) rings in the two complexes may have different conformations. The proven chair conformations for the B–(N–N)$_2$–Co rings [15] may severely restrict the access of molecular oxygen into the co-ordination sphere of the cobalt atom, whereas, with the ' Me_2Ga ' moiety incorporated in the ligands, the more likely planar Ga–(N–N)$_2$–Co rings may allow the oxygen molecule to interact more readily with the cobalt atom. [A planar arrangement for the Ga–(N–N)$_2$–Co six-membered rings in this tetrahedral complex would remove the severe steric interaction between a Ga–*Me* and the H(3) of a pz ring, inherent in a boat conformation. This situation is to be contrasted with that found in square-planar [Ni{$Me_2Ga(pz)_2\}_2$] where boat conformations for the Ga–(N–N)$_2$–Ni rings considerably reduce the steric interactions between adjacent pairs of pz H(3) atoms inherent in a system with planar Ga–(N–N)$_2$–Ni rings.]

Attempts to prepare the more sterically hindered complex [Co{$Me_2Ga(dmpz)_2\}_2$] produced an apparently air-stable purple solid but analytical results were consistently low (see Table 1) and attempts at recrystallization and sublimation failed to yield an analytically pure compound. The apparent resistance to attack by molecular oxygen in this complex probably stems from the shielding influence of the methyl substituents of the pz fragments positioned about the cobalt atom.

Zinc Complex.—Neither gallium ligand yielded a characterizable zinc complex and consequently the boron complex [Zn{$Me_2B(pz)_2\}_2$] was synthesized for comparative purposes. A noteworthy feature of this complex is that in solution the B–*Me* ^{1}H n.m.r. signal was temperature invariant, which suggests a likely planar arrangement for the B–(N–N)$_2$–Zn rings rather than rapidly flipping boat conformations for this tetrahedral complex. [A planar B–(N–N)$_2$–Zn ring removes the severe steric interaction between a B–*Me* and H(3) of a pz ring inherent in a tetrahedral complex incorporating B–(N–N)$_2$–Zn rings in boat conformations.] It is also profitable to compare the ^{1}H n.m.r. pattern displayed by the pz moieties in this complex with that observed for these groups in the corresponding square-planar nickel complex (see Table 2). In both complexes a doublet : doublet : triplet pattern was observed for the pz moieties with the doublets each displaying, in addition, a small cross-ring coupling of *ca.* 0·6 Hz. One of the two doublets was observed at different positions, whereas the other doublet appeared in essentially the same position in the two spectra. A plausible assignment is that H(5) adjacent to the boron atom will not shift position on changing the chelated metal atom whereas H(3) adjacent to the zinc or nickel atom experiences a shift in the two complexes. This observed shift is further evidence of a fundamentally different geometry for the two complexes.

Other Ligands.—The ligands [$Me_2B(dmpz)_2]^-$, [$Me_2Al(pz)_2]^-$, [$Al(pz)_4]^-$, [$H_2Ga(pz)_2]^-$, and [$Me_2In(pz)_2]^-$ have all been investigated for their potential chelating properties towards transition-metal ions but to date isolation of simple chelate complexes incorporating these ligands has not been achieved. Steric interactions inherent in the boron ligand [$Me_2B(dmpz)_2]^-$ may preclude formation of stable complexes, whereas with the aluminium ligands greater reactivity of both Al–C and Al–N bonds and a tendency to achieve higher co-ordination numbers [16] about the aluminium atoms may not favour the isolation of simple chelate complexes. The gallium hydride ligand [$H_2Ga(pz)_2]^-$ reacted vigorously with nickel and copper salts in thf solvent and hydrogen was briskly evolved. No complex

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* 1 B.M. ≃ 9·27 × 10^{-24} A m^2.

[14] D. J. Patmore, D. F. Rendle, A. Storr, and J. Trotter, *J.C.S. Dalton*, 1975, 718.

[15] L. J. Guggenberger, C. T. Prewitt, P. Meakin, S. Trofimenko, and J. P. Jesson, *Inorg. Chem.*, 1973, **12**, 508.

[16] N. N. Greenwood, B. P. Straughan, and B. S. Thomas, *J. Chem. Soc.* (*A*), 1968, 1248.

corresponding to the well characterized $[M\{H_2B(pz)_2\}_2]$ complexes[17] could be isolated. The greater reactivity of the Ga–H unit compared with the much less polar B–H unit (Allred–Rochow electronegativities: Ga, 1·82; B, 2·01; H, 2·1) may explain this difference in behaviour. Greater reactivity of both In–C and In–N bonds (compared with Ga–C and Ga–N bonds) could explain our inability to synthesize simple complexes of the pyrazolylindate ligand $[Me_2In(pz)_2]^-$, although it was noticeable that this ligand was much more slowly attacked by moist air than the corresponding aluminium ligand, $[Me_2Al(pz)_2]^-$.

EXPERIMENTAL

Air-sensitive materials were handled in a glove-box under an atmosphere of oxygen-free dry nitrogen or in a nitrogen-blanketed apparatus. Tetrahydrofuran (thf) was dried by heating under reflux over $Li[AlH_4]$ and then used immediately following distillation. Pyrazole and 3,5-dimethylpyrazole were used as purchased (K and K Laboratories). Trimethylboron (K and K Laboratories), and trimethylaluminium and triethylaluminium (Alfa Inorganics, Inc.) were vacuum distilled before use. Trimethylgallium,[18] trimethylindium,[18] and trimethylamine–gallane[19] were prepared as previously described. Sodium hydride was used as obtained (Alfa Inorganics, Inc.).

Preparative Details.—During the preparations of the ligands the course of the reaction was followed by monitoring the ^1H n.m.r. spectrum in the M–*Me* (M = B, Al, Ga, or In) region. The two species $Na[Me_3M(pz)]$ and $Na[Me_2M(pz)_2]$ gave M–Me signals separated by *ca.* 0·5 p.p.m. from each other, and consequently completion of the reaction could easily be ascertained.

Sodium dimethylbis(pyrazol-1-yl)gallate, $Na[Me_2Ga(pz)_2]$. Trimethylgallium (10·0 g, 87·2 mmol) in thf was added to sodium pyrazolide (87·2 mmol) [made from sodium hydride (2·09 g, 87·2 mmol) and pyrazole (5·93 g, 87·2 mmol) in thf solution] in the same solvent and the mixture was heated under reflux briefly. The resulting solution was cooled to room temperature and a solution of pyrazole (5·93 g, 87·2 mmol) in thf was added slowly and the mixture heated under reflux overnight. The solvent was removed *in vacuo* to leave the product as a white hygroscopic *solid*. In one preparation a three-fold excess of pyrazole was added in the last stage and the reaction mixture held at *ca.* 140 °C after removal of thf. The unchanged pyrazole was finally removed by sublimation *in vacuo* and elemental analysis showed the product to be $Na[Me_2Ga(pz)_2]$.

Tetramethylammonium dimethylbis(pyrazol-1-yl)gallate, $[Me_4N][Me_2Ga(pz)_2]$. A solution of $[Me_4N]Cl$ (0·20 g, 1·83 mmol) in a few cm^3 of methanol was added to $Na[Me_2Ga(pz)_2]$ (0·478 g, 1·86 mmol) in thf. Precipitated NaCl was removed by centrifuge and the solvent removed from the solution *in vacuo*. After washing with n-pentane the *solid* was recrystallized from acetone by diethyl ether addition.

Sodium bis(3,5-dimethylpyrazol-1-yl)dimethylgallate, $Na[Me_2Ga(dmpz)_2]$. Trimethylgallium (7·04 g, 61·4 mmol) in thf was added to sodium 3,5-dimethylpyrazolide (61·4 mmol) in thf and the mixture heated under reflux. After cooling to room temperature, 3,5-dimethylpyrazole (5·90 g, 61·4 mmol) in thf was added dropwise and the mixture then heated under reflux for 20 h to complete the reaction. After removal of solvent *in vacuo* the product remained as a white *solid*.

Tetraethylammonium bis(3,5-dimethylpyrazol-1-yl)dimethylgallate, $[Et_4N][Me_2Ga(dmpz)_2]$. This *salt* was prepared by using a similar procedure to that employed for $[Me_4N][Me_2Ga(pz)_2]$ above.

Sodium dimethylbis(pyrazol-1-yl)borate, $Na[Me_2B(pz)_2]$. Trimethylboron (4·0 g, 71·7 mmol) was condensed onto a solution of sodium pyrazolide (71·7 mmol) in thf cooled to −196 °C. The solution was allowed to warm to room temperature and then pyrazole (4·87 g, 71·6 mmol) in thf added dropwise. The solution was then heated under reflux for 24 h, but no reaction was evident as monitored by the ^1H n.m.r. spectrum. Consequently a further quantity of pyrazole (6 g, 88·2 mmol) was added and the thf solvent removed by distillation. The reaction mixture was then kept at *ca.* 200 °C for 24 h. At the end of this time complete conversion to $Na[Me_2B(pz)_2]$ was indicated by the ^1H n.m.r. spectrum. Excess of pyrazole was removed by sublimation to leave the product as a white *solid*.

Sodium bis(3,5-dimethylpyrazol-1-yl)dimethylborate, $Na[Me_2B(dmpz)_2]$. This was prepared by a similar method to that described above for $Na[Me_2B(pz)_2]$. Me_3B (5·10 g, 91·4 mmol) was treated with sodium 3,5-dimethylpyrazolide (91 mmol) in thf followed by addition of 3,5-dimethylpyrazole (12 g, 125 mmol), removal of solvent, and heating at *ca.* 200 °C until completion of the reaction.

Sodium dihydridobis(pyrazol-1-yl)gallate, $Na[H_2Ga(pz)_2]$. A solution of $Me_3N{\cdot}GaH_3$ (2·0 g, 15·2 mmol) in thf (30 cm^3) was added dropwise to a solution of sodium pyrazolide (15·2 mmol) in the same solvent, at room temperature. After stirring for 15 min, pyrazole (1·03 g, 15·2 mmol) in thf was added slowly. Rapid hydrogen evolution occurred. After 2 h, solvent was removed *in vacuo* to leave the product as a white *solid*. All subsequent handling of this material was carried out under N_2.

Attempts to prepare the copper and nickel complexes in thf solution were unsuccessful, rapid hydrogen evolution occurring as soon as the metal salt solution was added to the ligand solution.

Sodium dimethylbis(pyrazol-1-yl)aluminate, $Na[Me_2Al(pz)_2]$ *and sodium dimethylbis(pyrazol-1-yl)indate*, $Na[Me_2In(pz)_2]$. These two *salts* were prepared in a similar manner to the gallium analogue. Attempts to prepare similar transition-metal complexes, however, were not successful.

Sodium tetrakis(pyrazol-1-yl)aluminate, $Na[Al(pz)_4]$. Et_3Al (9·19 g, 80·7 mmol) In thf solution was added slowly to a solution of sodium pyrazolide (80·7 mmol) in the same solvent. Pyrazole (16·45 g, 242 mmol) in thf solution was then added slowly and the mixture heated under reflux. After removal of volatiles the product remained as an off-white *solid*. Attempts to prepare simple chelated transition-metal complexes using this ligand were unsuccessful.

Bis[dimethylbis(pyrazol-1-yl)gallato-N^{2}N$^{2'}$]nickel(II), $[Ni\{Me_2Ga(pz)_2\}_2]$. $Ni(BF_4)_2$ (0·68 g, 2·92 mmol) In thf was added to $Na[Me_2Ga(pz)_2]$ (1·5 g, 5·84 mmol) in the same solvent. Precipitated $NaBF_4$ was removed by the centrifuge and the solution evaporated to dryness under reduced pressure. The residue was extracted with CH_2Cl_2, and the resultant solution reduced to low volume followed by

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addition of light petroleum and cooling to yield orange crystals of the *product*, yield 0·6 g. The complex was also prepared by addition of an aqueous solution of $NiCl_2$ to an aqueous solution of $Na[Me_2Ga(pz)_2]$ (1 : 2 mol ratio of reactants). The precipitated product was extracted with diethyl ether and the extract solution evaporated to yield the crystalline *product*. The yield using this method was lower than that employing thf as solvent.

*Bis[dimethylbis(pyrazolyl)gallato-*N^{2}N$^{2'}$*]copper*(II), $[Cu\{Me_2Ga(pz)_2\}_2]$. Anhydrous copper(II) bromide (0·48 g, 2·15 mmol) in thf was treated with $Na[Me_2Ga(pz)_2]$ (1·10 g, 4·29 mmol) in the same solvent and the mixture stirred at room temperature to give a deep green solution. Precipitated NaBr was removed by filtration and the solution evaporated to dryness to give a mass of lilac *crystals*. These were recrystallized from CH_2Cl_2–pentane, yield 0·64 g.

*Bis[bis(3,5-dimethylpyrazol-1-yl)dimethylgallato-*N^{2}N$^{2'}$*]-copper*(II), $[Cu\{Me_2Ga(dmpz)_2\}_2]$. This complex was prepared as above from $Na[Me_2Ga(dmpz)_2]$ (1·84 g, 5·88 mmol) and $CuBr_2$ (0·60 g, 2·69 mmol) in thf solvent. The product was extracted with n-pentane, followed by evaporation to low volume and cooling to −20 °C to give a red crystalline *product*, yield 0·22 g.

*Bis[dimethylbis(pyrazol-1-yl)gallato-*N^{2}N$^{2'}$*]cobalt*(II), $[Co\{Me_2Ga(pz)_2\}_2]$. $Na[Me_2Ga(pz)_2]$ (0·496 g, 1·93 mmol) Was dissolved in deoxygenated water and mixed with $CoCl_2{\cdot}6H_2O$ (0·230 g, 0·97 mmol) in the same solvent. Immediate precipitation of the purple cobalt *complex* resulted. This was filtered off under nitrogen and dried *in vacuo*. Attempts at recrystallization from organic solvents were unsuccessful, and the material was used as originally precipitated. Both the solid complex and its solutions were extremely oxygen sensitive and all operations were carried out under nitrogen.

*Bis[dimethylbis(pyrazol-1-yl)borato-*N^{2}N$^{2'}$*]nickel*(II), $[Ni\{Me_2B(pz)_2\}_2]$. A solution of $Ni(BF_4)_2$ (0·85 g, 3·66 mmol) in thf was added to a solution of $Na[Me_2B(pz)_2]$ (1·45 g, 7·33 mmol) in the same solvent. After removal of precipitated $NaBF_4$ the solution was evaporated to dryness under reduced pressure. The residue was extracted with CH_2Cl_2 and the solution reduced to low volume followed by addition of light petroleum and cooling to yield the product as orange *crystals*. These were purified by recrystallization from CH_2Cl_2–light petroleum, yield 0·35 g.

*Bis[dimethylbis(pyrazol-1-yl)borato-*N^{2}N$^{2'}$*]copper*(II), $[Cu\{Me_2B(pz)_2\}_2]$. This complex was prepared by reacting $CuBr_2$ (0·90 g, 4·03 mmol) with $Na[Me_2B(pz)_2]$ (1·69 g, 8·55 mmol) in thf solvent. The blue solution formed initially was evaporated to dryness and the product extracted with CH_2Cl_2 followed by evaporation to low volume, addition of light petroleum, and cooling to give a lilac crystalline *product*. This was recrystallized from CH_2Cl_2–light petroleum, yield 0·75 g.

*Bis[dimethylbis(pyrazol-1-yl)borato-*N^{2}N$^{2'}$*]zinc*(II), $[Zn\{Me_2B(pz)_2\}_2]$. Anhydrous $ZnCl_2$ (0·62 g, 4·55 mmol) and $Na[Me_2B(pz)_2]$ (1·86 g, 9·40 mmol) were mixed in thf solvent. After removal of thf the residue was extracted with light petroleum and the resulting solution reduced to low volume and cooled to yield a white crystalline *product*. This was recrystallized from light petroleum, yield 0·5 g.

Spectra.—^{1}H N.m.r. spectra were obtained on Varian T60 and XL100 instruments. Mass spectra were recorded on a Varian MAT CH4-B mass spectrometer at 70 eV with the probe temperature at 110 °C.* High-resolution spectra were recorded on a modified A.E.I. MS9 instrument at 70 eV with a source temperature of 180 °C. Magnetic susceptibilities were measured on a Gouy balance. Solution spectra were measured on a Cary 14 spectrophotometer and solid-state spectra on a Spectronic 600 instrument with reflectance attachment.

Analysis.—The gallium hydride compound was analysed for hydrolysable hydrogen as previously described for such compounds.[19] Aluminium and gallium were determined gravimetrically as their quinolin-8-olates. C, H, And N analyses were made by Mr. P. Borda in the microanalytical laboratory at U.B.C.

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* 1 eV ≈ 1·60 × 10^{-19} J.