Spectroscopic Studies on Pyrazolyl-gallate and -borate Complexes of Copper(II) and Nickel(II)

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Variable-temperature ^{1}H n.m.r. data are presented for the square-planar Ni^{II} complexes, [{Me$_2$M(pz)$_2$}$_2$Ni] (M = Ga or B, and pz = pyrazolyl, $N_2C_3H_3$), and stereochemical nonrigidity for the molecules in solution is invoked to account for the spectral changes observed. Activation energies obtained for the suggested interconversion processes are 46 for the gallium and 67 kJ mol^{-1} for the boron complex. The Cu^{II} complexes, [{Me$_2$M(pz)$_2$}$_2$Cu] (M = Ga or B), and [{Me$_2$Ga(dmpz)$_2$}$_2$Cu] (dmpz = 3,5-dimethylpyrazolyl, $N_2C_5H_7$), have been studied by electronic absorption spectroscopy, ESCA, and e.s.r. spectroscopy. Data have been interpreted to provide tentative one-electron orbital sequences for copper in these complexes. The colour change observed from solid to solution for square-planar [{Me$_2$Ga(pz)$_2$}$_2$Cu] has been interpreted in terms of a tetrahedral distortion of the square-planar CuN$_4$ chromophore in solution. The e.s.r. results for the pseudotetrahedral complex, [{Me$_2$Ga-(dmpz)$_2$}$_2$Cu], indicate substantial *d–p* mixing in the ground state.

THERE have been numerous spectroscopic studies on transition-metal complexes incorporating pyrazolylborate ligands.[1-5] In contrast complexes involving as ligands pyrazolyl derivatives of the heavier Group III elements have not been reported with the exception of a preliminary crystal-structure study on the square-planar nickel complex, [{Me$_2$Ga(pz)$_2$}$_2$Ni] (pz = pyrazolyl).[6] As part of a general investigation into pyrazolyl derivatives of gallium and aluminium,[7,8] anionic chelating ligands have been synthesized and a number of their transition-metal complexes characterized.[9] We now describe some spectroscopic studies on pyrazolyl-gallate and -borate complexes of nickel(II) and copper(II). The current interest in the fluxional behaviour of pyrazolylborate transition-metal complexes [2-5] prompted a complete study of the nonrigidity of the [{Me$_2$Ga(pz)$_2$}$_2$Ni] complex in solution. The corresponding boron analogue has also been studied for its fluxionality, and the two examples represent the first such investigation for this type of bis(chelate) complex.

The stereochemistry,[10,11] electronic absorption spectra,[11] and magnetic properties [11] of copper(II) bis(chelates) have been the subject of considerable investigation. Generally, those containing the CuN$_4$ chromophore are square coplanar, stepped square-planar, tetrahedrally distorted square-planar, or pseudotetrahedral. The square-coplanar CuN$_4$ chromophore is exemplified in the copper phthalocyanine, copper porphyrins, and related systems. The stepped square-planar structure appears to be quite rare but an example is found in the [{Me$_2$Ga(pz)$_2$}$_2$Cu] complex,[12] and presumably in the analogous boron compound. Bis-(2,2′-bipyridylamine)copper(II) perchlorate [13,14] is typical of a tetrahedrally distorted square-planar CuN$_4$ system, whereas a pseudotetrahedral CuN$_4$ geometry has been shown for the complex [{Me$_2$Ga(dmpz)$_2$}$_2$Cu] [12] (dmpz = 3,5-dimethylpyrazolyl) and for bis(diethyl-3,3′,5,5′-tetramethyldipyrromethene-4,4′-dicarboxylato)copper-(II).[15] Hathaway [16] has discussed the electronic absorption spectra and the expected e.s.r. *g* values for such systems. A knowledge of the crystal structures of the copper complexes [12] together with the spectroscopic data collected in this study provide an ideal test of the diagnostics suggested by Hathaway [16] for distinguishing between a square-planar and a pseudotetrahedral CuN$_4$ chromophore.

Nickel Complexes.—Two square-planar nickel complexes, [{Me$_2$Ga(pz)$_2$}$_2$Ni] and [{Me$_2$B(pz)$_2$}$_2$Ni] have been characterized previously.[9] The present variable-

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

[2] J. L. Calderon, F. A. Cotton, and A. Shaver, *J. Organometallic Chem.*, 1972, **37**, 127; **38**, 105; **42**, 419.

[3] P. Meakin, S. Trofimenko, and J. P. Jesson, *J. Amer. Chem. Soc.*, 1972, **94**, 5677.

[4] A. R. Schoenberg and W. P. Anderson, *Inorg. Chem.*, 1974, **13**, 465.

[5] S. Trofimenko, *Inorg. Chem.*, 1970, **9**, 2493.

[6] D. F. Rendle, A. Storr, and J. Trotter, *J.C.S. Chem. Comm.*, 1974, 406.

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

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

[9] K. R. Breakell, D. J. Patmore, and A. Storr, *J.C.S. Dalton*, in the press.

[10] R. H. Holm and M. J. O'Connor, *Progr. Inorg. Chem.*, 1971, **14**, 241.

[11] B. J. Hathaway and D. E. Billing, *Co-ordination Chem. Rev.*, 1970, **5**, 143.

[12] D. J. Patmore, D. F. Rendle, A. Storr, and J. Trotter, *J.C.S. Dalton*, following paper.

[13] J. E. Johnson, T. A. Beineke, and R. A. Jacobson, *J. Chem. Soc.* (*A*), 1971, 1371.

[14] R. J. Dudley, B. J. Hathaway, and P. G. Hodgson, *J.C.S. Dalton*, 1972, 882.

[15] M. Elder and B. R. Penfold, *J. Chem. Soc.* (*A*), 1969, 2556.

[16] B. J. Hathaway, *J.C.S. Dalton*, 1972, 1196.

temperature ^1H n.m.r. study has demonstrated that the molecules are stereochemically non-rigid in solution. Figure 1 shows the room-temperature ^1H n.m.r. spectra of the two complexes. The expected doublet : doublet : triplet pattern for the protons on the pyrazolyl groups is observed and in the M*Me* region (M = Ga or B) two signals are featured, one at a position typical for non-transition-metal methyl derivatives of gallium and boron,[17] the second at much lower τ values. The crystal structure of the $[\{Me_2Ga(pz)_2\}_2Ni]$ complex [6] shows the Ga–(N–N)$_2$–Ni six-membered rings to be in boat conformations with one gallium atom positioned above and the other below the NiN_4 plane. This arrangement gives two gallium methyl groups in positions above and below the nickel atom in the NiN_4 plane, and it is these groups which are believed to give the abnormally low-field Ga*Me* signal by interaction with the transition metal. The remaining two gallium methyl groups are positioned away from the nickel environment and give a ^1H n.m.r. signal in the expected region. A similar argument may be put forward to explain the two B*Me* signals in the ^1H n.m.r. spectrum of the $[\{Me_2B(pz)_2\}_2Ni]$ complex. Trofimenko [18] has noted previously a downfield shift of half the methylene protons in the ^1H n.m.r. spectra of the boron derivatives, $[\{R_2B(pz)_2\}_2Ni]$ (R = Et or Bu^n), and postulated an interaction of these protons with the nickel atom to account for it. In direct contrast to the situation for these four nickel derivatives, a pronounced upfield shift for one of the methylene groups in the molybdenum complex, $[\{Et_2B(pz)_2\}Mo(CO)_2(\eta^3\text{-2-phenylallyl})]$, is observed in its ^1H n.m.r. spectrum.[5] Again, a boat conformation for the B–(N–N)$_2$–Mo ring was predicted, and Trofimenko suggested a strong interaction between the methylene group involved and the molybdenum atom to explain the anomalous ^1H n.m.r. signal. As further evidence of electron drift towards these methylene protons and towards the transition metal he cites the appearance of some abnormally low ν(CH) stretching frequencies in the i.r. spectrum of the complex in solution. Confirmation of these predictions has been recently forthcoming in the crystal-structure determination of the complex,[19] which demonstrated the existence of a novel C $\cdots$ H $\cdots$ Mo 3c–2e bond, and the authors predict that in solution the two methylene protons in close proximity to the molybdenum atom are involved in a rapid site-exchange to place them both at the same high-field position in the ^1H n.m.r. spectrum. In the square-planar nickel derivatives a similar multicentre bonding is not to be expected and the presence of electron density in nickel orbitals above and below the NiN_4 plane may in fact cause electron drift away from the C–H protons towards the carbon atoms, and hence cause a deshielding of these protons and move the pertinent ^1H n.m.r. signals to the observed low-field values.

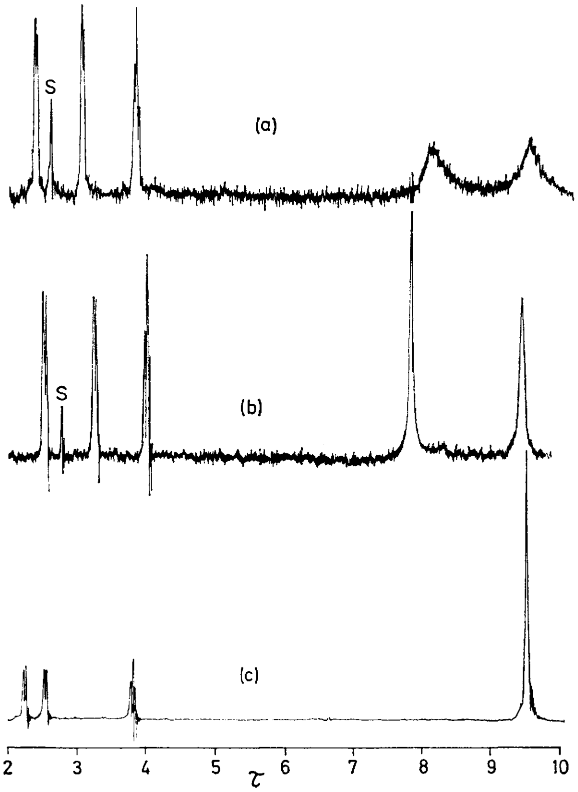

FIGURE 1 60 MHz Room-temperature ^1H n.m.r. spectra for $CDCl_3$ solutions (S = $CHCl_3$) of (a) $[Ni\{Me_2Ga(pz)_2\}_2]$, (b) $[Ni\{Me_2B(pz)_2\}_2]$, and (c) $[Zn\{Me_2B(pz)_2\}_2]$

In the present study stereochemical nonrigidity has been demonstrated for the $[\{Me_2Ga(pz)_2\}_2Ni]$ and $[\{Me_2B(pz)_2\}_2Ni]$ complexes by monitoring the M*Me* signals in the ^1H n.m.r. spectrum over a range of temperatures. On cooling solutions of the complexes the M*Me* signals sharpen and attain a maximum-separation value (1·67 for the boron, 1·51 p.p.m. for the gallium complex), whereas, on warming the solutions, the M*Me* signals broaden and eventually collapse into one signal at higher temperatures (coalescence temperatures: boron complex 100, gallium complex 70 °C). Figure 2 shows the variable-temperature ^1H n.m.r. spectrum for the gallium complex, and a similar spectrum was observed for the boron complex. The temperature dependence of the ^1H n.m.r. spectra can be explained on the basis of the stereochemical nonrigidity of the complexes. At low temperatures the ^1H n.m.r. spectra are believed to depict a situation similar to that observed in the solid state for the gallium complex. Thus the four methyl groups of the gallium (boron) occupy two unique environments, with two pseudo-axial on the M atoms, in close proximity to the nickel atom whereas the remaining two pseudo-equatorial on the M atoms, are positioned away from the nickel environment. On raising the temperature an interconversion process (Figure 3, for the gallium complex) is believed to occur, and, at a sufficiently high temperature, the rate of flipping of the six-membered M–(N–N)$_2$–Ni rings becomes rapid enough

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

[18] S. Trofimenko, *J. Amer. Chem. Soc.*, 1967, **89**, 6288.

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

to average out the MMe environments, concomitant with the appearance of one M*Me* ^1H n.m.r. signal. Similar stereochemical nonrigidity has been reported for the molybdenum complexes [$\{R_2B(pz)_2\}Mo(CO)_2(\pi\text{-}C_5H_5)$] (where $R_2 = Et_2$, pz_2 or pz, H) in which an inverting boat conformation for the B–(N–N)$_2$–Mo ring is postulated.[2] Stereochemical nonrigidity in complexes involving the terdentate chelate, tris-(1-pyrazolyl)borate ligand, $RB(pz)_3^-$, has also been demonstrated by ^1H n.m.r. methods. Substituted molybdenum[3] and manganese[4] carbonyl derivatives have been studied but in these cases internal rotation of the $RB(pz)_3^-$ groups about the boron–metal axis is postulated.

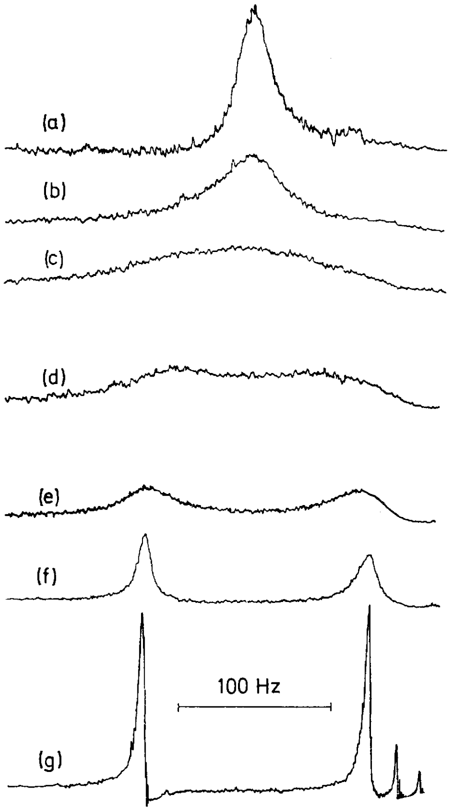

FIGURE 2 Variable-temperature ^1H n.m.r. spectrum of [$\{Me_2Ga(pz)_2\}_2Ni$] in $CDCl_3$ solution (Ga*Me* region); (a) 100, (b) 80, (c) 70, (d) 57, (e) 40, (f) 20, and (g) 0 °C

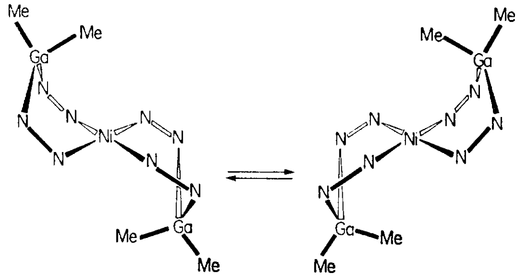

FIGURE 3 Suggested conformational equilibrium for [$\{Me_2Ga(pz)_2\}_2Ni$] complex in $CDCl_3$ solution (C_3H_3 fragments of pyrazolyl groups omitted for clarity)

The interconversion process (Figure 3) may proceed *via* a totally planar intermediate (with the exception of the methyl groups) with both M–(N–N)$_2$–Ni boats flipping synchronously, although with this mechanism a severe interaction between opposite pairs of H-3 atoms on the pyrazolyl moieties occurs in the planar intermediate. Alternatively, the boats may flip sequentially giving a crown configuration for the intermediate. In this arrangement, however, adverse steric interactions between pseudo-axial M-methyl groups will occur. It is possible that a mechanism between these two extremes may operate or that some twisting in the NiN_4 plane may occur in the transition stage which would relieve the adverse steric interactions. The energetics of the process were studied quantitatively by measuring the separation between the two MMe signals as a function of temperature. The method of Gutowsky and Holm[20] was then employed to obtain activation energies and entropies of activation for the interconversion processes. The values for these parameters are:

	E_a/kJ mol^{-1}	S/J K^{-1} mol^{-1}
[$\{Me_2Ga(pz)_2\}_2Ni$]	46 ± 4	−80 ± 8
[$\{Me_2B(pz)_2\}_2Ni$]	67 ± 8	−42 ± 20

The higher activation energy for the boron complex may be related to the shorter B–N as compared with the Ga–N distance in the M–(N–N)$_2$–Ni rings. This bond-length difference may introduce a greater barrier to boat-flipping in the boron complex than exists for the more symmetrical Ga–(N–N)$_2$–Ni boats. In addition, and as a consequence of the shorter B–N distance, there are more severe steric interactions between the boron–methyl groups and the adjacent H-5 atoms of the pyrazolyl fragments, which may restrict the interconversion process. Further evidence for a more rigid complex incorporating the pyrazolylborate ligands is obtained from the visible spectra listed in Table 1. Thus, the orange boron complex gives an orange solution when dissolved in pyridine, indicating little interaction between the nickel atoms and the solvent molecules. In contrast the orange gallium complex gives a blue solution in pyridine indicating the ready access of solvent molecules into the co-ordination sphere of the nickel atoms. The negative entropy values obtained for both complexes implies some ordering of the solvent in the intermediate stage of the interconversion processes.

A variable-temperature ^1H n.m.r. study of the tetrahedral zinc complex [$\{Me_2B(pz)_2\}_2Zn$] showed essentially no change in the singlet observed at room temperature for the B*Me* protons (Figure 1). It is therefore probable that planar B–(N–N)$_2$–Zn rings occur in this complex which, although more strained in themselves than boat conformations, nevertheless considerably reduce steric interaction inherent in a tetrahedral system with two boat conformations about the central metal atom. Alternatively, a system incorporating boat conformations for the B–(N–N)$_2$–Zn rings could be interconverting rapidly on the n.m.r. time-scale even at low temperatures, which again would mean one signal for B*Me* protons in the ^1H n.m.r. spectrum. The planar-ring

[20] H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, 1956, **25**, 1228.

hypothesis is more favoured and similar planar rings have already been proven crystallographically for the tetrahedral complex, $[\{Me_2Ga(dmpz)_2\}_2Cu]$,[12] and have been previously postulated for the $[\{Me_2Ga(pz)_2\}_2Co]$ tetrahedral complex.[9]

Copper Complexes.—Two square-planar copper complexes $[\{Me_2Ga(pz)_2\}_2Cu]$ and $[\{Me_2B(pz)_2\}_2Cu]$, and a pseudotetrahedral copper complex, $[\{Me_2Ga(dmpz)_2\}_2Cu]$, have been characterized previously.[9,12] Figure 4 shows the e.s.r. spectra for the compounds in light petroleum at −196 °C. The spin Hamiltonian parameters were obtained as follows. (*a*) The parallel components $A_{\parallel}^{Cu}$, $g_{\parallel}$ were obtained from the usual second-order analysis of the parallel features in Figure 4 indicated by $g_{\parallel}$. The spectra in Figure 4 also quite clearly show superhyperfine structure due to four equivalent (to within the linewidth) nitrogen atoms; the value of $A_{\perp}^{N}$ can also be obtained from the parallel features. (*b*) The values of $g_{\perp}$, $A_{\perp}^{Cu}$, and $A_{\parallel}^{N}$ are more difficult to obtain and a method indicated by the work of Guzy *et al.*[21] has been employed for $[\{Me_2B(pz)_2\}_2Cu]$ and $[\{Me_2Ga(pz)_2\}_2Cu]$. Thus the value of $g_{\perp}$ was obtained by measuring the position of the feature indicated in Figures 4(a) and 4(b). The value of $A_{\parallel}^{N}$ was obtained from the relation $X = (A_{\parallel}^{N} + A_{\perp}^{N})$ and $A_{\perp}^{Cu} = Y$ (see Figure 4). This method of analysis is quite approximate but in the absence of isotopic substitution and simulation of the observed spectra it can be deemed adequate. The method can be tested to some degree by a comparison of the observed and calculated magnetic moments $[\mu_{BM} = \frac{1}{3}(g_{\parallel} + 2g_{\perp})\sqrt{s(s+1)}]$. The calculated values are 1·81 for $[\{Me_2B(pz)_2\}_2Cu]$ and 1·82 for $[\{Me_2Ga(pz)_2\}_2Cu]$, in good agreement with experiment (see Table 1). The complete analysis of the e.s.r. spectrum of the tetrahedral complex, $[\{Me_2Ga(dmpz)_2\}_2Cu]$, is not possible because the principal directions of the hyperfine coupling constants of the nitrogen nuclei do not have any common directions with the principal directions of the g tensor and the copper hyperfine coupling. The parallel components $g_{\parallel}$ and $A_{\parallel}^{Cu}$ can be obtained as noted previously, whereas $g_{\perp}$ is obtained approximately from the position indicated by the arrow in Figure 4(c), and $A_{\perp}^{Cu}$ is *ca.* one-third of the linewidth in the perpendicular region. The calculated μ_{BM} is 1·85 compared with the experimental value of 1·87 (Table 1). Thus the g values obtained appear to be reasonable. The results of all these analyses are collected in Table 2.

TABLE 1

Electronic spectra of Cu^{II} and Ni^{II} complexes

	Sol. spectra					
	Cyclohexane		Pyridine		Reflectance spectra [a]	
Compound	$\nu_{max.}/cm^{-1}$	ε	$\nu_{max.}/cm^{-1}$	ε	$\nu_{max.}/cm^{-1}$	μ/B.M. [b]
$[\{Me_2B(pz)_2\}_2Cu]$	31 640	1 140				
	20 000	33	19 420	43 [c]	19 420	1·82
	16 950sh	25	16 807	43 [d]	17 090	
$[\{Me_2Ga(pz)_2\}_2Cu]$	29 580	1 185				
	15 380	93	15 625	81	19 800	1·84
	12 500sh	66			16 950	
$[\{Me_2Ga(dmpz)_2\}_2Cu]$	37 730	2 790				
	24 690	1 900			25 000	1·87
	20 200	1 970			19 610	
	11 980sh	71				
	9 380	160				
$[\{Me_2B(pz)_2\}_2Ni]$	37 310	1 740				
	21 370	65	21 370	64	20 800	0
$[\{Me_2Ga(pz)_2\}_2Ni]$	36 760	2 150				
	22 120	68	16 807	10	21 740	0

[a] Measured between 13 500 and 28 600 cm^{-1}. [b] Corrected for ligand and metal diamagnetism. [c] ε slowly decreases. [d] ε slowly increases.

TABLE 2

E.s.r. and derived data together with ESCA binding energies

Compound	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}^{Cu}$ [a]	$A_{\perp}^{Cu}$	$A_{\parallel}^{N}$	$A_{\perp}^{N}$	$-\chi$ [b]	α^2	$\left(\frac{\alpha'}{2}\right)^2$	N 1*s* [c]	Cu $2p^{\frac{1}{2}}$	Cu $2p^{\frac{3}{2}}$
$[\{Me_2B(pz)_2\}_2Cu]$	2·209	2·031	206	34	20·5	15·2	4·00	0·75	0·33	400·3	936·2	956·1
$[\{Me_2Ga(pz)_2\}_2Cu]$ [d]	2·213	2·029	206	35	21·0	15·0	4·04	0·75	0·33	400·3	936·1	956·3
$[\{Me_2Ga(pz)_2\}_2Cu]$ [e]	2·210	2·028	206	36	21·0	15·0	4·04	0·74	0·33			
$[\{Me_2Ga(dmpz)_2\}_2Cu]$	2·316	2·041	95	*ca.*50						400·1	935·4	955·3
[Cu(pc)] [f]	2·160	2·045	219	30	19·7	14·7	3·88	0·73	0·30	398·5	934·6	954·6
[Cu(tpp)] [g]	2·190	2·045	201	33	16·1	14·6	3·37	0·79	0·30			

[a] Hyperfine coupling constants in units of 10^4 $cm^{-1} = 10^6$ m^{-1}. [b] Atomic units of volume $= 0{\cdot}148168 \times 10^{-33}$ m^3; $\chi = \frac{4\pi}{S}\langle\psi|\sum_i \delta(r_i)S_{zi}|\psi\rangle$. [c] Binding energies in eV $= 1{\cdot}6021 \times 10^{-19}$ J. [d] Hyperfine parameters obtained from light petroleum at −196 °C. [e] Hyperfine parameter obtained from Cu-doped nickel isomorph at −196 °C; values at 27 °C are identical. [f] See ref. 21. [g] See P. T. Manoharan and M. T. Rogers, ' Electron Spin Resonance of Metal Complexes,' ed. T. F. Yen, Plenum, New York, 1969, p. 143.

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[21] C. M. Guzy, J. B. Raynor, and M. R. Symons, *J. Chem. Soc.* (*A*), 1969, 2299.

The e.s.r. spectra of the three Cu$^{\mathrm{II}}$ complexes in light petroleum solution at room temperature consisted of four ill-resolved resonances. The overall widths of the spectra indicated that both $A_{\|}^{\mathrm{Cu}}$ and $A_{\perp}^{\mathrm{Cu}}$ are of the same relative sign: the absolute sign being predicted to be negative on theoretical grounds.[22] The linewidths for solution are *ca.* 200, 85, and 72 G for $[\{\mathrm{Me_2Ga(pz)_2}\}_2\mathrm{Cu}]$, $[\{\mathrm{Me_2B(pz)_2}\}_2\mathrm{Cu}]$, and $[\{\mathrm{Me_2Ga(dmpz)_2}\}_2\mathrm{Cu}]$. These generally broad lines are no doubt a consequence of spin rotational effects due to the large *g*-anisotropy, an effect which has been observed previously in Cu(acac)$_2$ (acac = acetylacetonato),[23] although some $\mathrm{M_I}$-dependent variation could be detected for $[\{\mathrm{Me_2Ga(dmpz)_2}\}_2\mathrm{Cu}]$. The narrower linewidth in the case of this latter complex permitted the detection of nitrogen superhyperfine structure on the high-field line due to four equivalent nitrogen atoms, indicating that this complex, and presumably the two square-planar derivatives, are contiguous in solution. The dramatic difference in linewidths between the spectra of $[\{\mathrm{Me_2Ga(pz)_2}\}_2\mathrm{Cu}]$ and $[\{\mathrm{Me_2B(pz)_2}\}_2\mathrm{Cu}]$ and $[\{\mathrm{Me_2Ga(dmpz)_2}\}_2\mathrm{Cu}]$ can possibly be explained by the onset of an Orbach process due to low-lying excited states.[24] The electronic spectrum (see later) of $[\{\mathrm{Me_2Ga(pz)_2}\}_2\mathrm{Cu}]$ changes drastically in solution (relative to the solid-state spectrum) lending credence to this tentative suggestion. The shortened electronic T_1 also permits the detection of a broad proton ^{1}H n.m.r. signal for this complex in solution.[9]

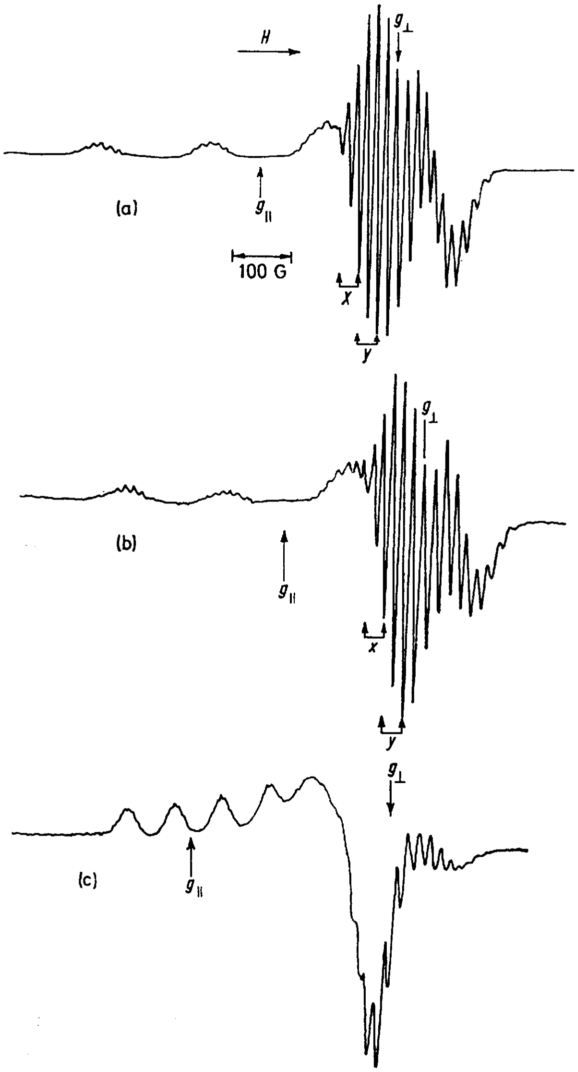

FIGURE 4 E.s.r. spectrum in light petroleum glass at −196 °C for (a) $[\{\mathrm{Me_2B(pz)_2}\}_2\mathrm{Cu}]$, (b) $[\{\mathrm{Me_2Ga(pz)_2}\}_2\mathrm{Cu}]$, and (c) $[\{\mathrm{Me_2Ga(dmpz)_2}\}_2\mathrm{Cu}]$

The binding energies obtained from the ESCA experiments are given in Table 2. Both the nitrogen 1*s* and the copper $2p^{1/2}$ and $2p^{3/2}$ binding energies in the pyrazolyl-borate and -gallate copper complexes are significantly higher than the corresponding values reported previously for copper phthalocyanine [Cu(pc)]. This is indicative of a somewhat more positive environment for both nitrogen and copper in the present complexes and may be related to their square-planar stepped and tetrahedral structures [12] as compared to the planar structure of the [Cu(pc)] derivative. The slight reduction in binding energies in $[\{\mathrm{Me_2Ga(dmpz)_2}\}_2\mathrm{Cu}]$ relative to $[\{\mathrm{Me_2B(pz)_2}\}_2\mathrm{Cu}]$ and $[\{\mathrm{Me_2Ga(pz)_2}\}_2\mathrm{Cu}]$ reflect the inductive effects of the methyl substituents on the pyrazolyl rings in this pseudotetrahedral complex and also the planar geometry of the Ga–(N–N)$_2$–Cu rings as compared to the boat conformations for M–(N–N)$_2$–Cu (M = B or Ba) in the square-planar complexes.[12]

The interpretation of the electronic spectral data and e.s.r. results obtained from polycrystalline samples (nickel isomorph and light petroleum glass at —196 °C) of the square-planar complexes $[\{\mathrm{Me_2B(pz)_2}\}_2\mathrm{Cu}]$ and $[\{\mathrm{Me_2Ga(pz)_2}\}_2\mathrm{Cu}]$ requires a knowledge of the ground state of the molecule. In order to proceed with the analysis we shall use the known crystal structures [6,12] and simple crystal-field arguments. A crystal-structure determination of the complex $[\{\mathrm{Me_2Ga(pz)_2}\}_2\mathrm{Cu}]$ shows that it possesses a stepped square-planar structure comparable to the isomorphic $[\{\mathrm{Me_2Ga(pz)_2}\}_2\mathrm{Ni}]$ structure,[6] with a step-angle of 33·7°.[12] The copper atoms occupy a centre of inversion in the $P2_1/c$ space group of the crystal. Owing to the fact that the Cu–N bond lengths from the two nitrogen atoms on a given dimethylbis-(1-pyrazolyl)gallate ligand are slightly different, the point group of the molecule is only C_i; however, if this slight bond-length difference (1·99 *vs.* 1·98 Å) is ignored, the point group is C_{2h}. Assuming C_{2h} symmetry the following molecular axes are adopted: *z* along the C_2 axis (in the CuN$_4$ plane), *x* in the mirror plane and in the plane of the CuN$_4$ chromophore, and *y* thus perpendicular to the CuN$_4$ plane (see Figure 3). The most likely one-electron orbital sequence is then: $d_{xz} \gg d_{z^2} > d_{x^2-y^2} > d_{yz} \approx d_{xy}$, based on simple crystal-field arguments. The presence of in- and out-of-plane π-bonding could well change the ordering of the d_{z^2},

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[22] See *e.g.* B. R. McGarvey, *J. Phys. Chem.*, 1967, **71**, 51.
[23] R. Wilson and D. Kivelson, *J. Chem. Phys.*, 1966, **44**, 4445.
[24] D. Kivelson, *J. Chem. Phys.*, 1966, **45**, 1324.

$d_{x^2-y^2}$, d_{yz}, and d_{xy} orbitals amongst themselves but the $^2B_g(d_{xz})$ ground state would appear to be clear cut. The foregoing qualitative ordering could also be further obfuscated by the fact that both d_{xz} and d_{yz} transform as B_g and the d_{z^2}, $d_{x^2-y^2}$ and d_{xy} all transform as A_g.

The hyperfine coupling constants of copper and nitrogen can be analysed in the usual way[22] to provide estimates of α^2 and $(\alpha'/2)^2$ where α and α' are the MO coefficients of Cu^{II} and N atomic orbitals respectively in the b_g odd-electron MO. The results are collected in Table 2 together with similar data for [Cu(pc)] and [Cu(tpp)] (tpp = tetraphenylporphyrin). The values of α^2 reflect the increasing ionic character of the bonding environment of the copper from the phthalocyanine to $[\{Me_2Ga(pz)_2\}_2Cu]$, in accord with the ESCA results. However, the nitrogen bonding parameters indicate a slightly more covalent environment for these atoms in $[\{Me_2Ga(pz)_2\}_2Cu]$ than in [Cu(pc)], a situation at variance with the ESCA result. This result reflects the dangers of attempting to assess overall covalency from variations of MO coefficients obtained from properties dependent on antibonding MO's (see ref. 25). The large value of χ (spin density at the copper nucleus) reflects polarization contributions of the inner A_g orbitals which also contain small contributions from the copper 4*s* orbitals.[22]

The *g* values obtained for $[\{Me_2Ga(pz)_2\}_2Cu]$ doped in the nickel isomorph together with the reflectance spectrum (Table 1) of this copper complex lead to a tentative assignment of the bands in the visible region. The broad band at 19 800 cm^{-1} is believed to contain the $d_{xz}\rightarrow d_{xy}$ and $d_{xz}\rightarrow d_{yz}$ transitions, whereas the band at 16 950 cm^{-1} contains the $d_{xz}\rightarrow d_{z^2}$ and $d_{xz}\rightarrow d_{x^2-y^2}$ transitions. A comparison of the *g* shift in the perpendicular direction with this assignment of the electronic spectrum suggests substantial interaction between ligand and metal orbitals in the $A_g(d_{z^2})$ and $A_g(d_{x^2-y^2})$ MO's. A similar assignment for the reflectance spectrum of the boron analogue, $[\{Me_2B(pz)_2\}_2Cu]$, is applicable.

The electronic absorption and e.s.r. data for $[\{Me_2Ga(pz)_2\}_2Cu]$ in solution present a somewhat different situation. As can be seen from Table 1 the electronic spectral properties of $[\{Me_2Ga(pz)_2\}_2Cu]$ in solution are quite different from those in the polycrystalline state (the complex is green in solution and violet in the solid). On the other hand the e.s.r. data (Table 2) are very similar for the compound in both the light petroleum glass and the nickel isomorph. In addition the green colour of a light petroleum solution does not change on cooling from room temperature to −196 °C. The interesting aspect of the electronic spectrum of $[\{Me_2Ga(pz)_2\}_2Cu]$ in solution relative to that for the polycrystalline state is the lowering of the energy of the *d–d* bands to 15 380 cm^{-1} with a shoulder at 12 500 cm^{-1}. At the same time there is only a small increase in the *g* values.* Hathaway[16] has pointed out that a tetrahedrally distorted square-planar CuN_4 chromophore can lead to electronic absorptions in the region 12 000—16 000 cm^{-1} with a shoulder occurring to low-frequency. The spectrum of $[\{Me_2Ga(pz)_2\}_2Cu]$ in solution (Table 1) displays these characteristic absorptions and a tetrahedrally distorted square-planar CuN_4 chromophore is therefore predicted for the complex in solution. This configurational change is no doubt accompanied by a flattening out of the $Ga-(N-N)_2-Cu$ six-membered rings to ease steric interactions. A similar configurational change does not appear to take place for the boron complex, $[\{Me_2B(pz)_2\}_2Cu]$. By analogy with the corresponding nickel complexes (see earlier) it is quite likely that a more rigid $M-(N-N)_2-Cu$ ring exists for M = B rather than for M = Ga, and in addition more severe steric interactions are inherent in the former. These features could explain the reluctance of this complex to interact with solvent molecules. Further support for the easier flattening-out of the $Ga-(N-N)_2-Cu$ rings in $[\{Me_2Ga(pz)_2\}_2Cu]$ is to be found in the spectral changes produced when the complexes are dissolved in pyridine (Table 1). The absorption spectrum of $[\{Me_2Ga(pz)_2\}_2Cu]$ in pyridine is typical of either tetragonal-octahedral CuN_6 or square-pyramidal CuN_5 geometry,[16] and we therefore consider the boat conformations for the $Ga-(N-N)_2-Cu$ rings have opened up sufficiently to permit access of pyridine molecules to the vacant copper co-ordination sites. In contrast the ' stiffer ' boron complex is slow to react with the pyridine solvent. The interaction of pyridine with the corresponding square-planar nickel derivatives has been discussed earlier, but note that $[\{Me_2B(pz)_2\}_2Ni]$ does not react whereas $[\{Me_2B(pz)_2\}_2Cu]$ interacts slowly. A slight structural change in the two complexes may account for this difference in behaviour, and supportive crystal-structure data on the analogous gallium complexes does reveal a significantly more open structure for $[\{Me_2Ga(pz)_2\}_2Cu]$ as compared with the $[\{Me_2Ga(pz)_2\}_2Ni]$ structure, with step angles of 33·7 and 39° for the two compounds.[12] The electronic absorption spectrum of $[\{Me_2Ga(pz)_2\}_2Cu]$ in solution can be interpreted as follows: the change to tetrahedrally distorted square-planar geometry will lead to an overall reduction in the mean energy of the *d–d* transitions so that the $d_{x^2-y^2}$ and d_{z^2} orbitals will become slightly stabilized or remain roughly unchanged whereas the d_{xy} and d_{yz} will be destabilized markedly. The 15 380 band is therefore assigned to the $d_{xz}\rightarrow d_{z^2}$ and $d_{xz}\rightarrow d_{x^2-y^2}$ transitions and the 12 500 cm^{-1} band to the $d_{xz}\rightarrow d_{xy}$ and $d_{xz}\rightarrow d_{yz}$ transitions. Such an assignment will lead to a small change in g_{yy} ($= g_{\parallel}$),[11] as observed, and to a larger change in g_{xx} and g_{zz}. The fact that hardly any change in $g_{\perp}$ is detected presumably reflects the increased covalent participation of the d_{xy} and d_{xz} orbitals offsetting the reduction in excitation energies.

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* The increase in $g_{\parallel}$ is experimentally significant since the mean error is $\pm 0{\cdot}002$ but that of $g_{\perp}$ is not, especially in view of the uncertainty of measuring this quantity from the e.s.r. spectra of glassy samples.

[25] J. I. Zink and R. S. Drago, *J. Amer. Chem. Soc.*, **1972**, **94**, 4550.

The pseudotetrahedral [{$Me_2Ga(dmpz)_2$}$_2$Cu] is one of the few examples [12] where e.s.r. has been detected for a copper system possessing a near-tetrahedral CuN_4 chromophore, others being bis-(α,α′-dibromodipyrromethene)copper(II) [26] and bis-(2,2′-bipyridylamine)-copper(II) diperchlorate.[14] The previous study [14] indicated that the anisotropy of the nuclear hyperfine parameters of tetrahedrally co-ordinated copper are substantially reduced from those in distorted octahedral environments. This reduction is due to the 4*p* and 3*d* contributions to the hyperfine coupling tensor tending to cancel each other if the 4*p* orbital admixture is sufficiently large.[27] In the present case, the data in Table 2 show the dramatic reduction in $A_{\|}^{Cu}$ and apparent increase in $A_{\perp}^{Cu}$ from square-planar to pseudotetrahedral geometry, due to the reduction of the anisotropy of the hyperfine coupling. There is also an increase in $g_{\|}$ and $g_{\perp}$, no doubt due to an overall lowering of the electronic transitions. The somewhat uncertain values of the hyperfine coupling tensors render an analysis for the bonding parameters inappropriate but the overall reduction of $A_{\|}^{Cu}$ is indicative of a fairly high degree of covalency together with a significant admixture of the 4*p* orbitals in the ground state. Further evidence for 4*p* admixture is to be found in the relatively narrow e.s.r. linewidths observed for this molecule as compared with the square-planar complexes. Bates [28] has shown previously that such mixing of 3*d* and 4*p* orbitals will lead to a somewhat longer electronic longitudinal-relaxation time (T_1).

The electronic absorption spectrum of [{$Me_2Ga(dmpz)_2$}$_2$Cu] is typical of a tetrahedral CuN_4 chromophore.[16] The assignment of the one-electron orbital sequence for the complex can be arrived at as follows: the molecule possesses a C_2 axis which will be designated *z*; neglecting the inclination of the ligand planes, for the moment, the CuN_4 chromophore is approximately an elongated tetrahedron [12] so that d_{xz} and d_{yz} are of comparable energy. If we now rotate one of the ligand planes in the *xy* plane toward the *y* axis to reduce the dihedral angle between the planes from 90° to the observed value of 72°,[12] it is apparent that the positive hole resides in an orbital dominated by d_{yz}. A tentative orbital sequence is thus: $d_{yz} \geqslant d_{xz} > d_{xy} \gg d_{z^2} > d_{x^2-y^2}$. The electronic absorption spectrum (Table 1) can now be assigned qualitatively as $d_{yz} \rightarrow d_{z^2}$ occurring at 9 380 cm^{-1} and $d_{yz} \rightarrow d_{x^2-y^2}$ occurring at 11 980 cm^{-1}, with the other possible transitions occurring to much lower energy.

We conclude that this study indicates that the diagnostics suggested by Hathaway [16] for distinguishing between a square-planar and a pseudotetrahedral CuN_4 system are reasonable for the present copper complexes, and can be useful in detecting structural changes between solution and the crystalline state.

EXPERIMENTAL

The complexes were prepared as reported previously.[9] Variable-temperature ^1H n.m.r. spectra were recorded on a Varian XL 100 spectrometer and the temperature controller was calibrated with ethylene glycol. Spectra were recorded for $CDCl_3$ solutions, except that of [{$Me_2B(pz)_2$}$_2$Ni] which was recorded for 1,2-dichloroethane solution in order to achieve a higher temperature without risk of bursting the sealed n.m.r. tube containing the sample. All solutions were made up under nitrogen and degassed *in vacuo* before the n.m.r. tube was flame-sealed.

Electronic solution spectra were recorded on a Cary 14 spectrometer by use of 1·0 cm solution cells, and reflectance spectra on a Spectronic 600 with finely ground samples. Magnetic susceptibilities were measured on a Gouy balance.

E.s.r. spectra at −196 °C of degassed 10^{-4}M light petroleum glasses of [{$Me_2B(pz)_2$}$_2$Cu], [{$Me_2Ga(pz)_2$}$_2$Cu], and [{$Me_2Ga(dmpz)_2$}$_2$Cu] were recorded on a Varian E 3 spectrometer operating at *X*-band. The magnetic-field strength was calibrated with p.m.r. probes and the microwave frequency was monitored on a Hewlett–Packard 5425 L counter. The spectrum of [{$Me_2Ga(pz)_2$}$_2$Cu] doped in the nickel isomorph, [{$Me_2Ga(pz)_2$}$_2$Ni], was also recorded at room temperature and at −196 °C but was identical to that obtained for the glass.

The *X*-ray photoelectron binding energies (ESCA) for polycrystalline samples of [{$Me_2B(pz)_2$}$_2$Cu], [{$Me_2Ga(pz)_2$}$_2$-Cu], [{$Me_2Ga(dmpz)_2$}$_2$Cu], and [Cu(pc)] were obtained on a Varian IEE 15 instrument equipped with a high-intensity magnesium anode and are relative to the C 1*s* binding energy in Scotch Tape (285·0 eV).

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