Crystal and Molecular Structures of Bis[dimethylbis-(1-pyrazolyl)-gallato]copper(II) and Bis[dimethylbis-(3,5-dimethyl-1-pyrazolyl)-gallato]copper(II)

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Crystals of (I) $[\{Me_2Ga(pz)_2\}_2Cu]$, (pz = pyrazolyl, $N_2C_3H_3$), are monoclinic, a = 8·522(3), b = 18·091(5), c = 7·463(3) Å, β = 105·90(4)°, space group $P2_1/c$, Z = 2. Crystals of (II) $[\{Me_2Ga(dmpz)_2\}_2Cu]$, (dmpz = 3,5-dimethylpyrazolyl, $N_2C_5H_7$), are monoclinic, a = 16·645(4), b = 12·964(1), c = 14·344(4) Å, β = 104·69(2)°, space group $I2/a$, Z = 4. Both structures were determined from diffractometer data by Patterson and Fourier syntheses, and refined by full-matrix least-squares methods to R 0·057 [(I), 1692 observed reflexions] and 0·047 [(II), 1995 observed reflexions]. The $[\{Me_2Ga(pz)_2\}_2Cu]$ molecule is in a pseudo-chair conformation with the two six-membered Ga–(N–N)$_2$–Cu rings in boat conformations. The copper atom lies on a crystallographic centre of symmetry in the middle of a planar arrangement of four nitrogen atoms. Mean dimensions are: Cu–N, 1·987, Ga–N 1·975, and Ga–C 1·962 Å; N–Ga–N 92·6, and N–Cu–N (chelate angle) 92·6°. Steric requirements of the ligands in $[\{Me_2Ga(dmpz)_2\}_2Cu]$ necessitate adoption of pseudotetrahedral geometry about the central copper atom, with dihedral angle 71·9° between the two N–Cu–N co-ordination planes, and an almost planar arrangement for the Ga–(N–N)$_2$–Cu six-membered rings. Mean dimensions are: Cu–N 1·959, Ga–N 1·996, and Ga–C 1·972 Å; N–Ga–N 103·3 and N–Cu–N (chelate angle) 104·9°.

THE crystal structures of numerous poly-(1-pyrazolyl)-borate (pz) transition-metal complexes have been reported. These include complexes incorporating the terdentate chelating ligands, $[HB(pz)_3]^-$,[1-4] and $[(pz)B(pz)_3]^-$,[5] in addition to those incorporating the bidentate chelating ligands, $[H_2B(pz)_2]^-$,[6] $[H_2B(dmpz)_2]^-$,[7,8] $[Et_2B(pz)_2]^-$,[9,11] and $[(pz)_2B(pz)_2]^-$.[12,13] In all of those reported the B–(N–N)$_2$–M (M = transition metal) six-membered rings are in boat conformations except for $[\{Et_2B(pz)_2\}(\eta^3\text{-}C_3H_5)(Hpz)(CO)_2Mo]$,[9] where a shallow chair conformation is adopted by the B–(N–N)$_2$–Mo ring to relieve steric interactions. In contrast, structural studies of pyrazolyl derivatives of the heavier Group III elements have received little attention. Two studies have been reported, the symmetrical dimer, $[\{D_2Ga(pz)\}_2]$,[14] and the nickel complex, $[\{Me_2Ga(pz)_2\}_2Ni]$.[15] In both these compounds the expected boat conformation for the Ga–(N–N)$_2$–M′ (where M′ = Ni or Ga) six-membered rings was established. We now extend our work in this area to include two copper complexes, (I) $[\{Me_2Ga(pz)_2\}_2Cu]$ and (II) $[\{Me_2Ga(dmpz)_2\}_2Cu]$ (dmpz = 3,5-dimethylpyrazolyl) and the results clearly demonstrate the sterically controlled geometry of the central CuN_4 unit. (I) Adopts a square-planar geometry for the CuN_4 feature and, as in the corresponding nickel complex,[15] steric interactions are kept to a minimum in the overall pseudo-chair conformation of the molecule which incorporates the Ga–(N–N)$_2$–Cu six-membered rings in boat conformations. More demanding steric requirements cause the adoption of a pseudotetrahedral geometry for the CuN_4 unit in (II), and also cause the adoption of an almost planar arrangement for the Ga–(N–N)$_2$–Cu six-membered rings. In addition to extending our structural studies in this area, the knowledge of the stereochemistry of the two CuN_4 chromophores has greatly facilitated the interpretation of spectroscopic data collected for the two compounds.[16]

EXPERIMENTAL

The complexes were prepared and characterized as described previously.[17]

Crystal Data.—(*a*) (I). $C_{16}H_{24}CuGa_2N_8$, $M = 531{\cdot}4$, Monoclinic, $a = 8{\cdot}522(3)$, $b = 18{\cdot}091(5)$, $c = 7{\cdot}463(3)$ Å, $\beta = 105{\cdot}90(4)°$, $U = 1106{\cdot}5$ Å^3, $D_m = 1{\cdot}58$, $Z = 2$, $D_c = 1{\cdot}595$, $F(000) = 534$. Space group $P2_1/c$ (C^5_{2h}, No. 14) from systematic absences. Cu-K_α radiation, $\lambda = 1{\cdot}5418$ Å; $\mu(\text{Cu-}K_\alpha) = 43{\cdot}7$ cm^{-1}.

(*b*) (II). $C_{24}H_{40}CuGa_2N_8$, $M = 643{\cdot}6$, Monoclinic, $a = 16{\cdot}645(4)$, $b = 12{\cdot}964(1)$, $c = 14{\cdot}344(4)$ Å, $\beta = 104{\cdot}69(2)°$, $U = 2994{\cdot}0$ Å^3, $D_m = 1{\cdot}43$, $Z = 4$, $D_c = 1{\cdot}428$, $F(000) = 1324$. Space group $I2/a$ (nonstandard setting of $C2/c$, C^6_{2h}, No. 15) from intensity statistics and successful refinement. $\mu(\text{Cu-}K_\alpha) = 33{\cdot}4$ cm^{-1}.

Crystals of (I) were lilac-coloured plates and the specimen used for data collection, with dimensions *ca.* 0·2 × 0·06 × 0·6 mm^3, was mounted with c^* parallel to the goniostat axis. Crystals of (II) were dark red parallelepipeds of which many proved to be twinned. An untwinned sample was

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[1] M. R. Churchill, K. Gold, and C. E. Maw, *Inorg. Chem.*, 1970, **9**, 1597.

[2] G. Avitabile, P. Ganis, and M. Nemiroff, *Acta Cryst.*, 1971, **B27**, 725.

[3] F. A. Cotton, B. A. Frenz, and A. Shaver, *Inorg. Chim. Acta*, 1973, **7**, 161.

[4] E. M. Holt, S. L. Holt, and K. J. Watson, *J.C.S. Dalton*, 1973, 2444.

[5] R. J. Restivo and G. Ferguson, *J.C.S. Chem. Comm.*, 1973, 847.

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

[7] C. A. Kosky, P. Ganis, and G. Avitabile, *Acta Cryst.*, 1971, **B27**, 1859.

[8] F. A. Cotton, M. Jeremic, and A. Shaver, *Inorg. Chim. Acta*, 1972, **6**, 543.

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

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

[11] F. A. Cotton and V. W. Day, *J.C.S. Chem. Comm.*, 1974, 415.

[12] J. L. Calderon, F. A. Cotton, and A. Shaver, *J. Organometallic Chem.*, 1972, **37**, 127.

[13] E. M. Holt and S. L. Holt, *J.C.S. Dalton*, 1973, 1893.

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

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

[16] F. G. Herring, D. J. Patmore, and A. Storr, preceding paper.

[17] K. R. Breakell, D. J. Patmore, and A. Storr, *J.C.S. Dalton*, 1975, in the press.

found with dimensions *ca.* 0·4 × 0·4 × 0·6 mm^3, and was subsequently used for data collection with c^* parallel to the goniostat axis. For both compounds, oscillation, Weissenberg, and precession photographs were used to determine the space groups and unit-cell dimensions. Accurate cell dimensions were obtained from a least-squares fit of 20 [for (I)] and 17 [for (II)] $\sin^2\theta$ (hkl) values, measured on a General Electric XRD 6 Datex-automated diffractometer with Cu-K_α radiation. The space group of (I) was determined uniquely by systematic absences to be $P2_1/c$, but in the case of (II) the systematic absences hkl when $h + k + l = 2n + 1$, and $h0l$ when $h = 2n + 1$ gave a choice between space groups $I2/a$ and Ia [nonstandard settings of $C2/c$, C_{2h}^6, No. 15 and Cc, C_s^4, No. 9].

Intensity data for both compounds were collected on a Datex-automated General Electric XRD 6 diffractometer by use of the θ—2θ scan method at a rate of 2° min^{-1} in 2θ. Cu-K_α radiation was used and a scintillation counter equipped with a nickel filter and pulse-height analyser ensured that the radiation was approximately monochromatic. For (I) 1992 and for (II) 2701 independent reflexions were measured with $2\theta \leqslant 135°$ of which 1692 (I) and 1995 (II) reflexions having $I > 3\sigma(I)$ were considered observed. The variance of the intensity $\sigma^2(I)$ is defined as $S + B + (dS)^2$ where S is the scan count, B the background count, and d a factor to account for instrument instability, set at 0·07 for (I) and 0·08 for (II). A standard reflexion monitored periodically during each data collection was used to scale the respective sets of data. Structure amplitudes were derived in the usual way, and no absorption corrections were applied to either set of data because of the relatively small size of the crystals used, and in the case of (I) because of the irregular nature of a number of the crystal faces.

Structure Analysis.—(*a*) (I). The unit cell dimensions of (I) proved to be very similar to those of [{Me$_2$Ga(pz)$_2$}$_2$Ni],[15] which, together with a similar intensity distribution, indicated that the two compounds were isomorphous. The final atomic co-ordinates of the non-hydrogen atoms in the nickel isomorph were input to structure-factor calculations for the copper isomorph, and gave R 0·179. Refinement of the structure was by full-matrix least-squares methods with anisotropic thermal parameters for the non-hydrogen atoms. A difference-Fourier synthesis computed with R at 0·071 revealed the pyrazolyl ring hydrogen atoms but the methyl hydrogen-atom positions were not clearly resolved. The pyrazolyl-ring hydrogen atoms were included in the refinement with isotropic thermal parameters and the methyl hydrogen atoms were placed in calculated positions assuming ideal sp^3 geometry at the carbon atoms and C–H 1·0 Å. Eight reflexions $(-1,-1,1;$ $-2,-3,1;$ $-1,-7,1;$ $1,0,0;$ $0,2,0;$ $0,8,0;$ $0,2,1;$ and $1,5,1)$ which were considered to suffer from either extinction effects or instrumental error were given zero weight at this stage in the refinement. Convergence was reached with R 0·057 and R' $(= \Sigma w(F_o - F_c)^2/\Sigma wF_o^2)$ 0·073. The average and largest shift-to-error ratios in the refined parameters were 0·16 and 1·6 respectively. A final difference-Fourier synthesis showed no fluctuations >0·81 eÅ^{-3}.

(*b*) (II). Intensity statistics indicated that the centrosymmetric space group $I2/a$ was the most likely choice, and a three-dimensional Patterson synthesis yielded initial co-ordinates for the copper and gallium atoms consistent with this choice. With $Z = 4$, in $I2/a$, crystallographic two-fold symmetry is imposed on the molecule, **and** the copper and both gallium atoms were found to **lie on** the

TABLE 1

Final positional (fractional × 10^4) parameters * with estimated standard deviations in parentheses. Hydrogen atoms are numbered according to the carbon atom to which they are bonded

(*a*) (I) [{Me$_2$Ga(pz)$_2$}$_2$Cu]

	x	y	z
Ga	−2997(1)	−1172(1)	−2692(1)
Cu	0	0	0
N(1)	390(5)	−1057(2)	−484(5)
N(2)	−706(5)	−1494(2)	−1716(6)
N(3)	−1158(5)	188(2)	−2644(5)
N(4)	−2365(5)	−246(2)	−3711(5)
C(1)	1796(6)	−1432(3)	66(7)
C(2)	1636(7)	−2119(3)	−807(9)
C(3)	56(8)	−2133(3)	−1896(9)
C(4)	−895(7)	738(3)	−3724(7)
C(5)	−1949(8)	672(4)	−5492(8)
C(6)	−2836(8)	47(4)	−5404(8)
C(7)	−3736(8)	−921(4)	−497(9)
C(8)	−4086(10)	−1815(4)	−4779(11)
H(1)	2716(70)	−1178(24)	931(74)
H(2)	2642(138)	−2653(48)	−580(143)
H(3)	−630(96)	−2462(40)	−2855(104)
H(4)	−6(73)	1082(28)	−3234(74)
H(5)	−1870(146)	943(55)	−6417(155)
H(6)	−3294(158)	−279(60)	−5677(164)
H(7A)	−2909	−590	355
H(7B)	−3856	−1383	197
H(7C)	−4806	−658	−886
H(8A)	−3392	−1857	−5700
H(8B)	−5174	−1617	−5468
H(8C)	−4221	−2330	−4331

(*b*) (II) [{Me$_2$Ga(dmpz)$_2$}$_2$Cu]

	x	y	z
Ga(1)	2500	100(1)	0
Ga(2)	2500	5947(1)	0
Cu	2500	3031(1)	0
N(1)	1879(3)	1060(3)	656(3)
N(2)	2039(2)	2100(3)	802(3)
N(3)	1561(2)	4998(3)	−565(3)
N(4)	1542(2)	3942(2)	−487(3)
C(1)	1370(4)	769(4)	1203(4)
C(2)	1196(4)	1609(4)	1700(5)
C(3)	1624(3)	2430(4)	1435(4)
C(4)	1674(5)	3530(4)	1767(5)
C(5)	804(3)	5339(4)	−1026(4)
C(6)	282(3)	4499(4)	−1246(4)
C(7)	757(3)	3637(4)	−907(3)
C(8)	490(4)	2536(4)	−989(5)
C(9)	1090(8)	−333(6)	1238(9)
C(10)	623(6)	6456(5)	−1227(9)
C(11)	2183(7)	6627(6)	1091(8)
C(12)	1669(6)	−586(7)	−1031(7)
H(2)	862(39)	1622(47)	2137(46)
H(6)	−313(39)	4552(44)	−1593(42)
H(4A)	2176(40)	3875(46)	1766(41)
H(4B)	1566(35)	3607(45)	2334(44)
H(4C)	1305(33)	3995(42)	1254(39)
H(8A)	6(40)	2453(58)	−1434(47)
H(8B)	953(41)	2137(48)	−1136(46)
H(8C)	407(45)	2243(63)	−397(60)
H(9A)	789(60)	−463(68)	1601(64)
H(9B)	791(84)	−483(93)	654(92)
H(9C)	1539(81)	−765(86)	1268(87)
H(10A)	998(77)	6983(81)	−931(88)
H(10B)	172(60)	6544(72)	−1786(71)
H(10C)	259(61)	6697(69)	−872(66)
H(11A)	1727(71)	6931(75)	984(79)
H(11B)	2373(65)	6114(89)	1671(75)
H(11C)	2460(74)	7114(90)	1334(84)
H(12A)	1501(82)	−1241(114)	−875(89)
H(12B)	1437(84)	−173(119)	−1422(112)
H(12C)	1829(65)	−769(81)	−1567(81)

two-fold symmetry axis. A structure-factor calculation based on these three atoms gave R 0·32. A difference-Fourier synthesis revealed the remainder of the non-hydrogen atom positions. Full-matrix least-squares refinement of these atoms with anisotropic thermal parameters reduced R to 0·071. All hydrogen atoms were located in a subsequent difference-Fourier synthesis and were refined with isotropic thermal parameters. On the difference map the highest peaks corresponded to the pyrazolyl H-4 atoms. The hydrogens of the pyrazolyl 3-Me groups were the next most clearly resolved, *i.e.* those hydrogens attached to C(4) and C(8). The remaining methyl hydrogen atoms, *i.e.* those on C(9)—(12) were located, but with less certainty. In contrast the hydrogen atoms of the gallium methyl groups in the square-planar complex (I) were not located. The refined C–H distances in both compounds lie in the range 0·71—1·27 Å, mean 0·95 Å. Examination of the observed and calculated structure factors revealed what appeared to be quite a serious extinction effect, and an extinction coefficient was therefore introduced. Refinement of this parameter produced a final coefficient of $5·9(4) \times 10^{-7}$. In spite of this correction six reflexions were given zero weight in the refinement, owing to severe extinction effects or suspected instrumental error (−4,0,2; −16,0,2; −3,−2,1; −1,−4,1; 0,0,2; and 0,0,12). Refinement converged with R 0·047 and R' 0·070. The average and largest shift-to-error ratio in the refined parameters were 0·18 and 1·92 respectively. A final difference-Fourier synthesis showed maximum fluctuations of ±0·76 e$Å^{-3}$.

TABLE 2

Final thermal parameters * ($Å^2 \times 10^4$) with estimated standard deviations in parentheses

(*a*) (I)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ga	448(4)	419(4)	568(4)	−42(2)	96(3)	−39(2)
Cu	430(5)	328(5)	373(5)	−2(3)	75(4)	6(3)
N(1)	478(21)	384(20)	416(20)	89(16)	101(16)	31(16)
N(2)	531(22)	312(19)	539(23)	13(16)	110(18)	−28(17)
N(3)	607(24)	332(19)	438(21)	−18(17)	114(18)	38(16)
N(4)	526(22)	421(21)	408(21)	−7(17)	74(17)	−29(16)
C(1)	463(26)	560(30)	515(28)	98(23)	134(22)	88(23)
C(2)	676(34)	480(28)	753(36)	234(25)	269(29)	111(27)
C(3)	754(36)	354(26)	733(36)	99(24)	239(30)	−44(24)
C(4)	716(34)	425(27)	510(28)	28(24)	206(25)	76(22)
C(5)	750(37)	640(34)	451(29)	110(29)	159(25)	138(26)
C(6)	630(34)	684(38)	428(27)	90(27)	26(24)	52(25)
C(7)	615(34)	779(41)	788(41)	94(31)	283(30)	109(34)
C(8)	861(46)	742(45)	941(51)	−190(37)	−64(37)	−307(38)

	U_{iso}/Å²		U_{iso}/Å²
H(1)	0·04(1)	H(4)	0·05(1)
H(2)	0·14(3)	H(5)	0·14(4)
H(3)	0·10(2)	H(6)	0·16(5)

(*b*) (II)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ga(1)	732(6)	276(4)	740(6)	0	295(5)	0
Ga(2)	539(5)	293(4)	842(7)	0	245(4)	0
Cu	489(5)	262(5)	723(7)	0	269(5)	0
N(1)	646(25)	290(18)	715(26)	−24(16)	316(22)	48(17)
N(2)	518(21)	332(19)	611(24)	2(16)	221(19)	−16(16)
N(3)	490(23)	269(17)	773(27)	28(15)	177(20)	19(17)
N(4)	503(21)	276(17)	615(23)	3(15)	181(18)	17(16)
C(1)	744(35)	426(26)	787(36)	−53(24)	371(31)	110(25)
C(2)	701(35)	575(30)	717(36)	−14(26)	385(31)	76(26)
C(3)	519(27)	430(23)	567(28)	33(20)	184(23)	9(21)
C(4)	790(41)	490(31)	637(38)	46(27)	271(33)	−62(26)
C(5)	567(30)	439(26)	834(36)	141(23)	161(27)	100(26)
C(6)	479(29)	571(31)	768(37)	28(24)	109(26)	27(26)
C(7)	569(29)	471(25)	481(26)	−80(22)	173(23)	−53(21)
C(8)	554(34)	512(30)	737(39)	−123(25)	94(31)	−25(26)
C(9)	1197(70)	536(37)	1342(81)	−171(42)	737(68)	116(43)
C(10)	774(49)	489(37)	1483(80)	222(34)	11(56)	141(42)
C(11)	912(57)	611(41)	1218(71)	44(39)	336(51)	−329(45)
C(12)	1022(57)	686(44)	837(51)	−293(41)	230(46)	−237(40)

	U_{iso}/Å²		U_{iso}/Å²
H(2)	0·08(2)	H(9C)	0·18(5)
H(6)	0·08(2)	H(10A)	0·18(5)
H(4A)	0·07(2)	H(10B)	0·10(3)
H(4B)	0·07(2)	H(10C)	0·12(3)
H(4C)	0·06(1)	H(11A)	0·14(4)
H(8A)	0·08(2)	H(11B)	0·17(4)
H(8B)	0·08(2)	H(11C)	0·18(5)
H(8C)	0·10(3)	H(12A)	0·13(5)
H(9A)	0·11(3)	H(12B)	0·24(7)
H(9B)	0·17(6)	H(12C)	0·09(4)

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

In both analyses the weighting scheme used was $\sqrt{w} = 1/\sigma(F)$. Scattering factors for gallium, copper, nitrogen, and carbon were taken from ref. 18 and those for hydrogen from ref. 19. Those for gallium and copper were corrected for the real and imaginary parts of anomalous dispersion.[20] Measured and calculated structure amplitudes are listed in Supplementary Publication No. SUP 21239 (44 pp., 1 microfiche).* Final positional and thermal parameters are given in Tables 1 and 2.

DISCUSSION

The stereochemistry of a large number of bis(bidentate chelate)copper(II) complexes has been reviewed.[21] The results of the present analyses clearly illustrate the importance of steric factors in determining the geometry of the central CuN_4 moiety in the complexes, and the stereoscopic views of the two molecules, given in Figure 1, depict the square-planar and pseudotetrahedral arrangements encountered about the copper atoms. Mean distances and angles for the molecules are given in Figure 2, individual distances and angles in Table 3, selected least-squares planes and dihedral angles in Table 4, and some non-bonded intramolecular distances for (II) in Table 5. Table 6 collects selected distances and angles for the pyrazolylgallate structures determined to date.

The complex (I) is isostructural with the corresponding nickel complex[15] and displays the familiar stepped square-planar structure about the central copper atom. The Ga–(N–N)$_2$–Cu six-membered rings are in boat conformations with one boat above and one below the CuN_4 plane. This arrangement is preferred over a totally planar system (planar with the exception of the Ga–Me groups) since steric interaction between the H-3 atoms on opposite pyrazolyl moieties are considerably reduced and there is less angular strain about the bow-split gallium atoms. The arrangement still allows a planarity about the nitrogen atoms,

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* For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1974, Index issue.

[18] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[19] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

[20] D. T. Cromer and D. Liberman, *J. Chem. Phys.*, 1970, **53**, 1891.

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

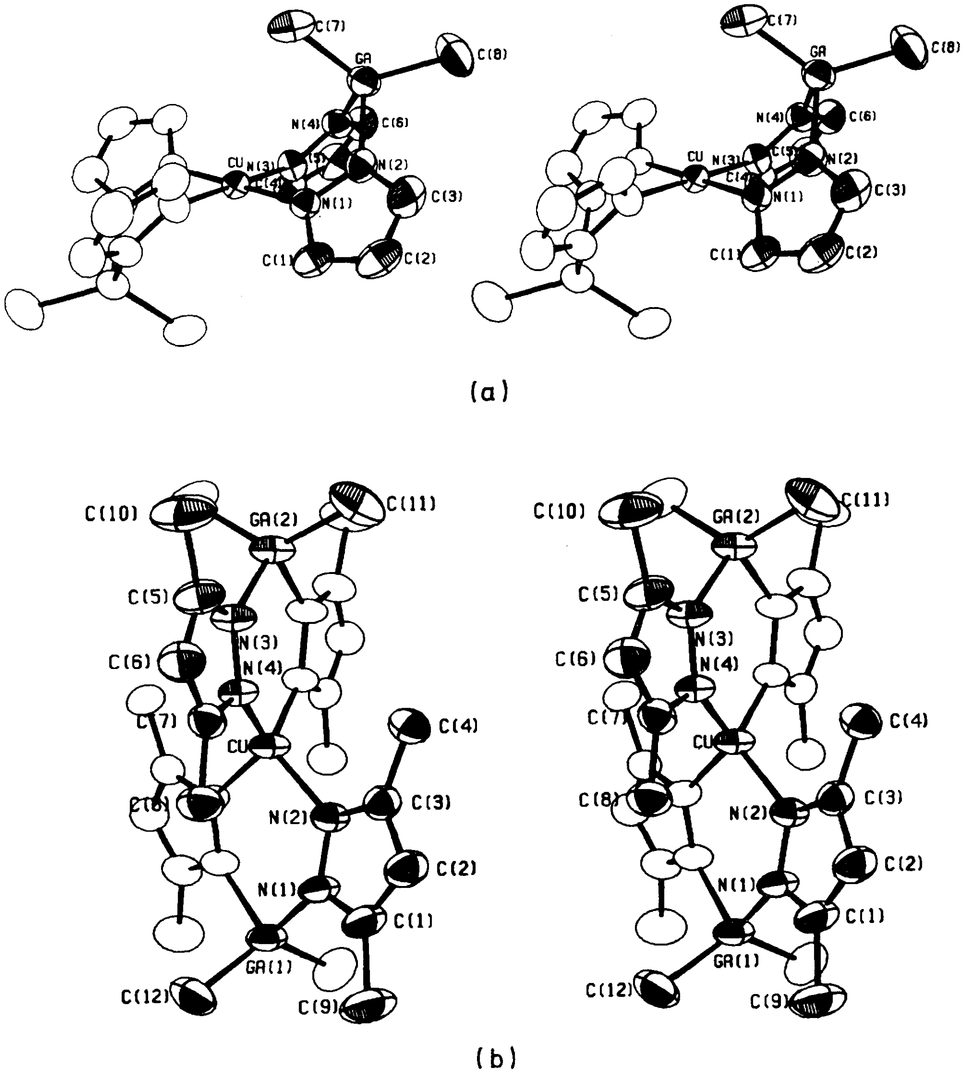

FIGURE 1 Stereoscopic view of (a) (I), and (b) (II)

and for the pyrazolyl moieties [see Table 4(*a*)], with the result that possible delocalization of 6π electrons in each ' N_2C_3 ' ring can give added stability to the complex. The boats adopted in this copper complex appear to be shallower than those in the corresponding nickel complex, as is evident from the smaller step-angle of 33·7° and step distance of 1·51 Å in the copper compound compared to the corresponding values of 39·0° and 1·65 Å for the [$\{Me_2Ga(pz)_2\}_2Ni$] derivative. The mean Cu–N distance of (1·987 Å) is close to the corresponding distance of 2·022 Å reported recently for the bis-[2-(2-methyl)pyridine]copper(II) iodide complex [22] which also contains a planar CuN_4 moiety. Further dimensional comparisons for this complex are given in Table 6.

The [$\{Me_2Ga(dmpz)_2\}_2Cu$] complex (II) is believed to be the most nearly tetrahedral reported for this type of CuN_4 bis(chelate) complex, with a dihedral angle of 71·9° between the two N–Cu–N co-ordination planes. A regular tetrahedral stereochemistry for complexes of the copper(II) ion is unknown but a number of complexes are known which involve a pseudotetrahedral geometry.[21,23] A number of such complexes involving the CuN_4 moiety, and containing two bidentate chelate groups, have been reported [24–26] with dihedral angles between the two N–Cu–N co-ordination planes ranging between 55·6 and 68°. The general influence of ligand stereochemistry on the nature of copper(II) co-ordination geometry has also been extensively investigated crystallographically on a number of salicylaldimine complexes [21,27–29] which again contain two bidentate chelate

[22] V. C. Copeland and D. J. Hodgson, *Inorg. Chem.*, 1973, **12**, 2157.

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

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

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

[26] C. H. Wei, *Inorg. Chem.*, 1972, **11**, 2315.

[27] P. O. Orioli and L. Sacconi, *J. Amer. Chem. Soc.*, 1966, **88**, 277.

[28] T. P. Cheeseman, D. Hall, and T. N. Waters, *J. Chem. Soc. (A)*, 1966, 685.

[29] E. N. Baker, G. R. Clark, D. Hall, and T. N. Waters, *J. Chem. Soc. (A)*, 1967, 251.

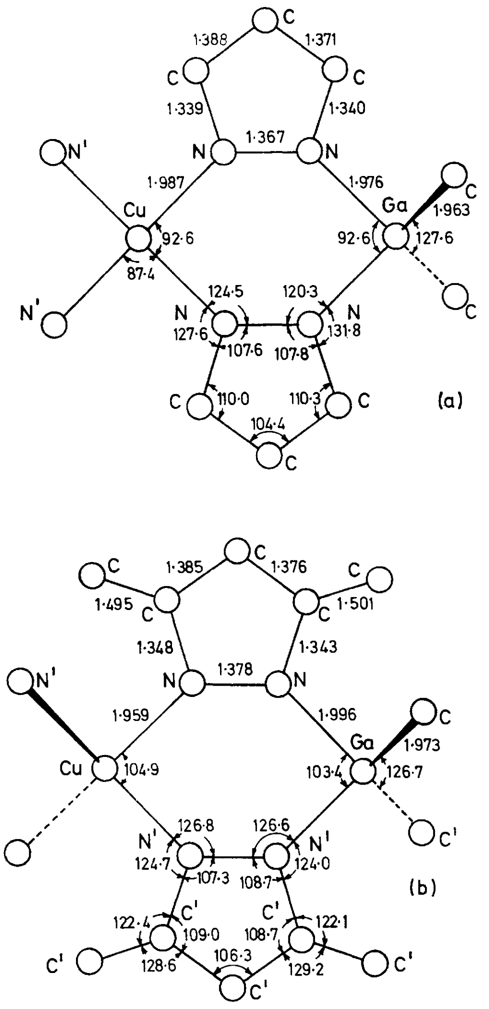

FIGURE 2 Mean dimensions for (a) (I), and (b) (II)

TABLE 3

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

(*a*) In (I)

(i) Bond distances

Ga–N(2)	1·976(4)	N(1)–C(1)	1·340(7)
Ga–N(4)	1·975(4)	N(2)–C(3)	1·351(7)
Ga–C(7)	1·963(7)	N(3)–C(4)	1·338(7)
Ga–C(8)	1·962(8)	N(4)–C(6)	1·328(7)
Cu–N(1)	1·994(4)	C(1)–C(2)	1·392(8)
Cu–N(3)	1·980(4)	C(2)–C(3)	1·370(9)
N(1)–N(2)	1·368(6)	C(4)–C(5)	1·383(8)
N(3)–N(4)	1·365(6)	C(5)–C(6)	1·372(10)

(ii) Valency angles

N(2)–Ga–N(4)	92·6(2)	N(1)–N(2)–C(3)	107·6(4)
C(7)–Ga–C(8)	127·6(3)	Cu–N(3)–N(4)	125·0(3)
N(2)–Ga–C(7)	105·8(2)	Cu–N(3)–C(4)	127·5(4)
N(2)–Ga–C(8)	108·8(3)	N(4)–N(3)–C(4)	107·5(4)
N(4)–Ga–C(7)	108·0(2)	Ga–N(4)–N(3)	120·4(3)
N(4)–Ga–C(8)	108·5(2)	Ga–N(4)–C(6)	131·5(4)
N(1)–Cu–N(3)	92·6(2)	N(3)–N(4)–C(6)	107·9(4)
N(1)–Cu–N(3′)	87·4(2)	N(1)–C(1)–C(2)	110·1(5)
Cu–N(1)–N(2)	124·0(3)	C(1)–C(2)–C(3)	104·4(5)
Cu–N(1)–C(1)	127·6(3)	N(2)–C(3)–C(2)	110·2(5)
N(2)–N(1)–C(1)	107·6(4)	N(3)–C(4)–C(5)	109·8(5)
Ga–N(2)–N(1)	120·1(3)	C(4)–C(5)–C(6)	104·3(5)
Ga–N(2)–C(3)	132·0(4)	N(4)–C(6)–C(5)	110·4(5)

TABLE 3 (*Continued*)

(*b*) In (II)

(i) Bond distances

Ga(1)–N(1)	1·999(4)	Ga(2)–N(3)	1·993(4)
Ga(1)–C(12)	1·965(10)	Ga(2)–C(11)	1·980(10)
Cu–N(2)	1·953(4)	Cu–N(4)	1·965(4)
N(1)–N(2)	1·380(5)	N(2)–C(3)	1·344(6)
N(3)–N(4)	1·376(5)	N(3)–C(5)	1·341(7)
N(1)–C(1)	1·347(8)	N(4)–C(7)	1·352(7)
C(1)–C(2)	1·372(8)	C(1)–C(9)	1·510(10)
C(2)–C(3)	1·386(8)	C(3)–C(4)	1·499(7)
C(5)–C(6)	1·379(8)	C(5)–C(10)	1·492(9)
C(6)–C(7)	1·384(8)	C(7)–C(8)	1·491(8)

(ii) Valency angles

C(12)–Ga(1)–C(12′)	126·1(6)	N(2)–Cu–N(4)	100·2(2)
N(1)–Ga(1)–N(1′)	103·0(2)	N(2)–Cu–N(4′)	124·5(2)
N(1)–Ga(1)–C(12)	106·7(3)	Ga(1)–N(1)–N(2)	125·2(3)
N(1)–Ga(1)–C(12′)	106·1(3)	Ga(1)–N(1)–C(1)	125·3(3)
C(11)–Ga(2)–C(11′)	127·2(4)	C(1)–N(1)–N(2)	108·1(4)
N(3)–Ga(2)–N(3′)	103·7(2)	Cu–N(2)–N(1)	127·2(3)
N(3)–Ga(2)–C(11)	104·9(3)	Cu–N(2)–C(3)	123·2(3)
N(3)–Ga(2)–C(11′)	106·9(3)	N(1)–N(2)–C(3)	107·5(4)
N(2)–Cu–N(2′)	103·7(2)	Ga(2)–N(3)–N(4)	127·9(3)
N(4)–Cu–N(4′)	106·1(2)	Ga(2)–N(3)–C(5)	122·7(3)
N(4)–N(3)–C(5)	109·3(4)	C(2)–C(3)–C(4)	129·4(5)
Cu–N(4)–C(7)	126·1(3)	N(2)–C(3)–C(4)	121·4(5)
Cu–N(4)–N(3)	126·4(3)	N(3)–C(5)–C(6)	108·2(5)
N(3)–N(4)–C(7)	107·1(4)	N(3)–C(5)–C(10)	122·2(6)
N(1)–C(1)–C(2)	109·1(5)	C(6)–C(5)–C(10)	129·5(6)
N(1)–C(1)–C(9)	122·0(6)	C(5)–C(6)–C(7)	106·6(5)
C(2)–C(1)–C(9)	128·9(7)	N(4)–C(7)–C(6)	108·8(4)
C(1)–C(2)–C(3)	106·1(5)	N(4)–C(7)–C(8)	123·3(5)
C(2)–C(3)–N(2)	109·2(4)	C(6)–C(7)–C(8)	127·8(5)

TABLE 4

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

(*a*) $[\{Me_2Ga(pz)_2\}_2Cu]$

Plane (1): N(1), N(2), C(1)—(3)

$$0{\cdot}5210X + 0{\cdot}3961Y - 0{\cdot}7561Z = -0{\cdot}2708$$

[Ga −0·153(1), Cu 0·271(1), N(1) 0·000(4), N(2) 0·001(4), C(1) −0·002(5), C(2) 0·003(6), C(3) −0·003(6)]

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

$$0{\cdot}4725X + 0{\cdot}3075Y - 0{\cdot}8259Z = -0{\cdot}0018$$

[Ga −0·001(1), Cu 0·002(1), N(1) −0·096(4), N(2) 0·070(4), C(1) −0·118(5), C(2) 0·039(6), C(3) 0·145(6)]

Plane (3): N(3), N(4), C(4)—(6)

$$0{\cdot}7865X - 0{\cdot}5538Y - 0{\cdot}2734Z = -0{\cdot}0161$$

[Ga 0·143(1), Cu 0·016(1), N(3) −0·004(4), N(4) 0·003(4), C(4) 0·007(6), C(5) −0·003(7), C(6) −0·003(7)]

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

$$0{\cdot}8116X - 0{\cdot}5138Y - 0{\cdot}2781Z = 0{\cdot}0001$$

[Ga 0·001(1), Cu −0·000(1), N(3) −0·009(4), N(4) −0·050(4), C(4) 0·056(6), C(5) 0·034(7), C(6) −0·031(7)]

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

$$0{\cdot}9522X + 0{\cdot}2471Y - 0{\cdot}1797Z = 0{\cdot}0$$

Plane (6): N(1)—(4)

$$0{\cdot}7791X - 0{\cdot}0854Y - 0{\cdot}6211Z = 0{\cdot}7574$$

[Ga −0·937(1), Cu −0·757(1), N(1) −0·042(4), N(2) 0·044(4), N(3) 0·045(4), N(4) −0·044(4)]

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

$$0{\cdot}1915X - 0{\cdot}4634Y - 0{\cdot}8652Z = 2{\cdot}2715$$

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

$$-0{\cdot}3714X + 0{\cdot}7920Y - 0{\cdot}4845Z = 0{\cdot}0$$

[Ga 0·000(1), Cu −0·000(1), C(7) −0·003(7), C(8) −0·009(8)]

TABLE 4 (*Continued*)

Dihedral angles (°) between planes

(1)–(2)	7·0	(2)–(4)	117·1
(3)–(4)	2·7	(5)–(8)	94·4
(5)–(6)	33·7	(6)–(7)	43·4
(5)–(7)	102·9		

(*b*) $[\{Me_2Ga(dmpz)_2\}_2Cu]$

Plane (1): Cu, N(2), N(2′)

$-0{\cdot}7243X - 0{\cdot}6894Z = -3{\cdot}0143$

Plane (2): Cu, N(4), N(4′)

$0{\cdot}4310X - 0{\cdot}9024Z = 1{\cdot}7935$

Plane (3): N(1), N(2), N(1′), N(2′)

$-0{\cdot}6594X - 0{\cdot}7518Z = -2{\cdot}7437$

[N(1) 0·154(4), N(2) −0·138(4), N(1′) −0·154(4), N(2′) 0·138(4), Ga(1) −0·000(1), Cu 0·000(1)]

Plane (4): N(3), N(4), N(3′), N(4′)

$0{\cdot}4636X - 0{\cdot}8861Z = 1{\cdot}9289$

[N(3) 0·066(4), N(4) −0·057(4), N(3′) −0·066(4), N(4′) 0·057(4), Ga(2) −0·000(1), Cu 0·000(1)]

Plane (5): Ga(1), Cu, N(1), N(2)

$-0{\cdot}6593X + 0{\cdot}0010Y - 0{\cdot}7519Z = -2{\cdot}7414$

[Ga(1) −0·002(1), Cu 0·002(1), N(1) 0·153(4), N(2) −0·138(4)]

Plane (6): Ga(2), Cu, N(3), N(4)

$0{\cdot}4636X - 0{\cdot}0005Y - 0{\cdot}8860Z = 1{\cdot}9264$

[Ga(2) −0·001(1), Cu 0·001(1), N(3) 0·066(4), N(4) −0·057(4)]

Plane (7): N(1), N(2), C(1)—(3)

$-0{\cdot}6216X + 0{\cdot}2105Y - 0{\cdot}7545Z = 2{\cdot}1945$

[N(1) 0·000(4), N(2) −0·000(4), C(1) −0·001(6), C(2) 0·001(6), C(3) −0·000(5), C(4) −0·024(7), C(9) −0·041(13), Ga(1) −0·365(1), Cu 0·435(1)]

Plane (8): N(3), N(4), C(5)—(7)

$0{\cdot}4730X - 0{\cdot}0908Y - 0{\cdot}8764Z = 1{\cdot}4270$

[N(3) −0·001(4), N(4) 0·000(4), C(5) 0·004(6), C(6) −0·004(6), C(7) 0·001(5), C(8) 0·034(7), C(10) 0·008(12), Ga(2) −0·159(1), Cu 0·185(1)]

Plane (9): N(1′), N(2′), C(1′)—(3′)

$-0{\cdot}6216X - 0{\cdot}2105Y - 0{\cdot}7545Z = -2{\cdot}9791$

Plane (10): N(3′), N(4′), C(5′)—(7′)

$0{\cdot}4730X + 0{\cdot}0908Y - 0{\cdot}8764Z = 2{\cdot}5098$

Plane (11): Ga(1), Cu, N(1), N(2), C(1)—(3)

$-0{\cdot}6547X + 0{\cdot}0025Y - 0{\cdot}7559Z = -2{\cdot}7197$

[Ga(1) −0·004(1), Cu 0·005(1), N(1) 0·143(4), N(2) −0·146(4), C(1) 0·253(6), C(2) 0·043(6), C(3) −0·205(5)]

Plane (12): Ga(2), Cu, N(3), N(4), C(5)—(7)

$0{\cdot}4677X - 0{\cdot}0011Y - 0{\cdot}8839Z = 1{\cdot}9397$

[Ga(2) −0·002(1), Cu 0·002(1), N(3) 0·058(4), N(4) −0·064(4), C(5) 0·114(6), C(6) 0·015(6), C(7) −0·087(5)]

Plane (13): Ga(1), Cu, N(1′), N(2′), C(1′)—(3′)

$-0{\cdot}6547X - 0{\cdot}0025Y - 0{\cdot}7559Z = -2{\cdot}7289$

Plane (14): Ga(2), Cu, N(3′), N(4′), C(5′)—(7′)

$0{\cdot}4677X + 0{\cdot}0011Y - 0{\cdot}8839Z = 1{\cdot}9529$

Plane (15): Ga(1), C(12), C(12′)

$0{\cdot}8176X - 0{\cdot}5758Z = 3{\cdot}4021$

Plane (16): Ga(2), C(11), C(11′)

$-0{\cdot}8534X - 0{\cdot}5213Z = -3{\cdot}5512$

Dihedral angles (°) between planes

(1)–(2)	71·9	(11)–(13)	179·7
(5)–(7)	12·2	(12)–(14)	179·9
(6)–(8)	5·2	(15)–(16)	113·4
(7)–(9)	24·3	(16)–(4)	86·2
(8)–(10)	10·4	(15)–(7)	96·1

* The orthogonalization matrix is:

$$\begin{pmatrix} X \\ Y \\ Z \end{pmatrix} = \begin{pmatrix} a & 0 & c\cos\beta \\ 0 & b & 0 \\ 0 & 0 & c\sin\beta \end{pmatrix} \quad \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

groups and display the CuN_2O_2 central unit. The dihedral angles between the two O–Cu–N co-ordination planes in these complexes are consistently less than 60°. In addition, an example of a bis(chelate) ' CuS_4 ' system having a pseudotetrahedral geometry has been reported recently.[30] No dihedral angle was quoted but from the atomic co-ordinates listed an angle of 75·4° between the two S–Cu–S co-ordination planes may be calculated. Data are summarized in Table 7 which also includes representative examples of square-planar copper(II) bis(chelate) complexes with dihedral angles of zero. The geometry of the present pseudotetrahedral complex (II) is dictated by the nature of the chelating ligands. A stepped square-planar structure is not possible in this case owing to the unfavourable steric interactions between the 3-methyl groups on opposite pyrazolyl moieties. The pseudotetrahedral geometry imposed on the complex [Figure 1(b)] removes these steric interactions by staggering the four 3-methyl groups about the copper atom. In addition a near-planar arrangement is imposed on the $Ga-(N-N)_2-Cu$ six-membered rings to remove the adverse steric effects between gallium-methyl and the 3-methyl groups which would be inherent if these rings adopted the more common boat conformations. Presumably the strain imposed on the near-planar six-membered rings is more than compensated for by the reduction in adverse steric interactions in the observed structures. It is interesting to contrast this structure with some related pyrazolyl complexes. The only bis(bidentate chelate) pyrazolylborate complex to be crystallographically characterized is the cobalt complex, $[\{H_2B(pz)_2\}_2Co]$. This has a tetrahedrally co-ordinated cobalt atom, but in this case the incorporation of the much less sterically demanding $[H_2B(pz)_2]^-$ ligands enables the six-membered $B-(N-N)_2-Co$ rings to adopt the much more common boat conformations. However, in the tetrahedral complexes, $[\{Me_2Ga(pz)_2\}_2M]$ (M = Zn or Co), the gallium-methyl groups are believed to cause planar conformations for the $Ga-(N-N)_2-M$ rings to relieve steric interactions.[17] A further example of the importance of steric effects in this type of complex has been reported by Cotton *et al.*[9] Thus, in the compound $[\{Et_2B(pz)_2\}(\eta^3-C_3H_5)(Hpz)(CO)_2Mo]$, the $B-(N-N)_2-Mo$ six-membered ring adopts a chair conformation, a very uncommon arrangement for this type of complex and one imposed on the molecule by severe steric interactions.

TABLE 5

Selected intramolecular non-bonded distances (Å) in (II)

Ga(1) · · · C(9)	3·331(9)	Cu · · · C(8)	3·348(6)
Ga(1) · · · C(1)	2·986(5)	C(3) · · · C(8)	3·514(9)
Ga(2) · · · C(10)	3·241(9)	C(4) · · · C(7)	3·756(9)
Ga(2) · · · C(5)	2·941(6)	Cu · · · Ga(1)	3·799(1)
Cu · · · C(4)	3·241(7)	Cu · · · Ga(2)	3·780(1)
Cu · · · C(3)	2·915(5)	Cu · · · C(11)	4·987(9)
Cu · · · C(7)	2·969(5)	Cu · · · C(12)	5·007(9)
C(9) · · · C(12)	3·64(2)	C(10) · · · C(11)	3·67(2)

The influence of steric interactions in determining the

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[30] H. van der Meer, *J.C.S. Dalton*, 1973, 1.

structures of pyrazolylgallate complexes may be judged by considering a number of the parameters collected in Table 6. The larger the V-angle observed for a particular complex the flatter the boat conformation for the Ga–(N–N)$_2$–M (M = Ga, Ni, or Cu) six-membered rings, until at 180° a planar arrangement is attained. The trend to flatter boats, and eventually planarity, is thought to be the result of increasing steric demands within the complexes. Increasing steric requirements are also reflected in a trend to larger values for the N–Ga–N and N–M–N angles, and also in a trend to larger Ga · · · M non-bonded distances. In the dimethylgallium derivatives, an approach to equal C(Ga) · · · M non-bonded distances reflects increasing steric demands within the complexes and the approach to planarity for the Ga–(N–N)$_2$–M rings. In the complexes [{Me$_2$Ga(pz)}$_2$] and (II), where there is the largest steric influence on the molecular geometry the Ga–N distances are longer than in the other complexes listed in Table 6, and also longer than that found normally in four-co-ordinate gallium complexes.[31,32] This may reflect a tendency to reduce steric interactions by both a lengthening of the Ga–N bond and by a flattening of the boat conformations in these two complexes. The

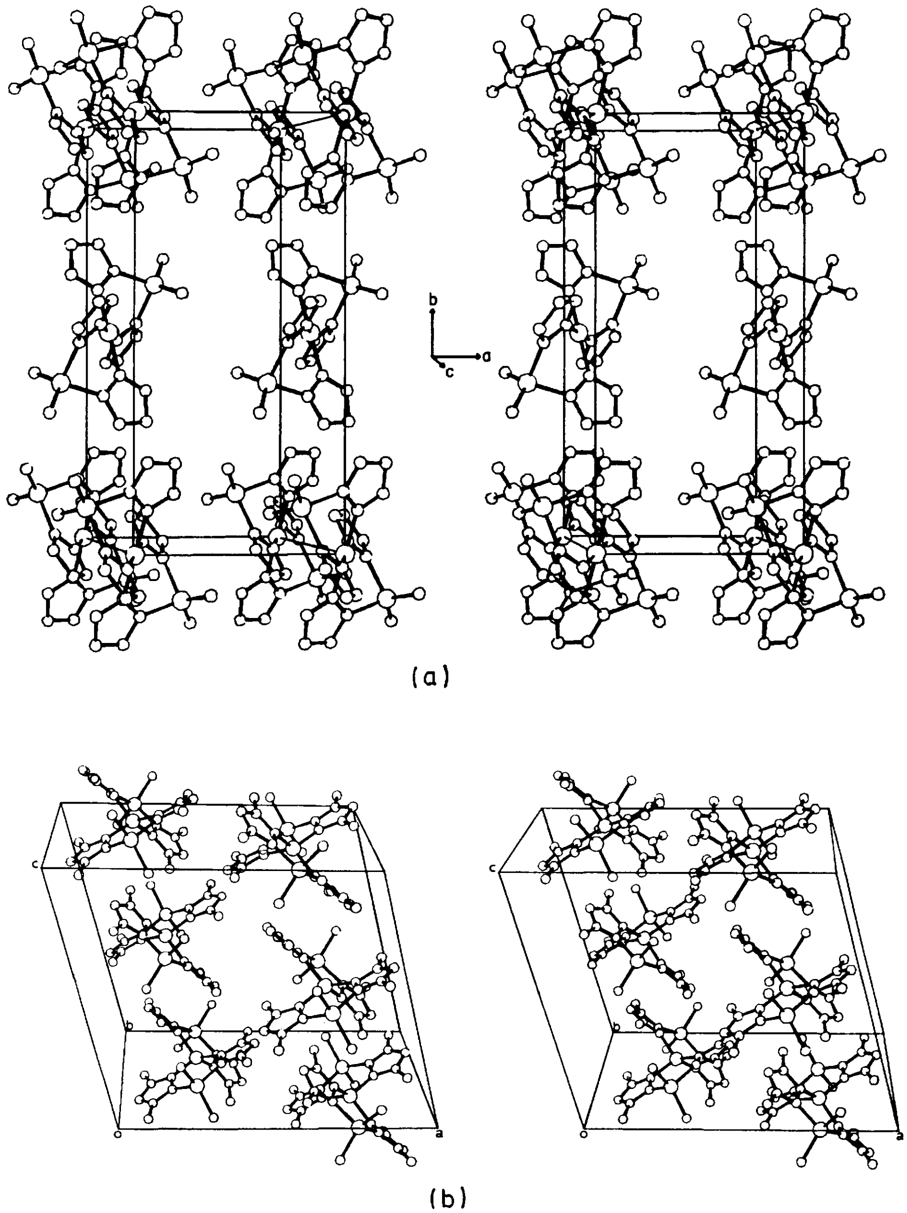

FIGURE 3 Stereoscopic view of the unit cell in (a) (I), and (b) (II)

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[31] D. F. Shriver and C. E. Nordman, *Inorg. Chem.*, 1963, **2**, 1298.

[32] W. Harrison, A. Storr, and J. Trotter, *J.C.S. Dalton*, 1972, 1554.

TABLE 6

Selected distances (Å) and angles (°) for known pyrazolylgallate structures

	Distance					Angle			
Compound	Ga–N	M–N	Ga · · · M	C(Ga) · · · M	Step	N–Ga–N	N–M–N	Step-angle [a]	V-angle [b]
$[\{D_2Ga(pz)\}_2]$ [c]	1·974		3·529			96·6			128·4
$[\{Me_2Ga(pz)\}_2]$ [d]	1·996		3·652	4·188, 5·385		96·1			131·5
$[\{Me_2Ga(pz)_2\}_2Ni]$ [e]	1·977	1·895	3·432	3·553, 5·271	1·65	91·6	92·4	39·0	116·4
$[\{Me_2Ga(pz)_2\}_2Cu]$ [f]	1·975	1·987	3·501	3·523, 5·371	1·51	92·6	92·6	33·7	117·1
$[\{Me_2Ga(dmpz)_2\}_2Cu]$ [f]	1·996	1·959	3·790	4·997		103·3	104·9		180

[a] See ref. 21. [b] Dihedral angle between two connected M, Ga, pz planes (see Tables 4 for copper complexes). [c] Ref. 14. [d] D. F. Rendle, A. Storr, and J. Trotter, unpublished results. [e] Ref. 15. [f] This work.

shorter Cu–N distance in the pseudotetrahedral compared to the square-planar complex may reflect lesser steric demands about the copper atom in the former molecule, although a change in hybridization about the transition metal may also be important.

TABLE 7

Dihedral angles (°) between the co-ordination planes in some four-co-ordinate copper(II) bis(chelates)

Chelating ligand	Central moiety	Angle
Salicylaldimine [a]	CuN_2O_2	0
N-Ethylsalicylaldimine [b]	CuN_2O_2	35·6
N-Butylsalicylaldimine [c]	CuN_2O_2	53·6
N-Propylsalicylaldimine [d]	CuN_2O_2	59·7
Dimethyl bis-(1-pyrazolyl)gallate [e]	CuN_4	0
2*H*-Pyrrole-2-carbaldimine [f]	CuN_4	0
2,2′-Bipyridylamine [g]	CuN_4	55·6
N-Butylpyrrole-2-carbaldimine [h, i]	CuN_4	60·1
N-Butylpyrrole-2-carbaldimine [i, j]	CuN_4	61·3
Dipyrromethene [k]	CuN_4	68
Dimethyl bis-(3,5-dimethyl-1-pyrazolyl)gallate [e]	CuN_4	71·9
Pyrrolidonecarbodithioate [l]	CuS_4	0
2,5-Dithiahexane-1,6-dicarboxylic acid [m]	CuS_4	75·4

[a] E. N. Baker, D. Hall, and T. N. Waters, *J. Chem. Soc.* (*A*), 1966, 680. [b] Monoclinic form; ref. 29. [c] Ref. 28. [d] Ref. 27. [e] This work. [f] R. Tewari and R. C. Srivastava, *Acta Cryst.*, 1971, **B27**, 1644. [g] Ref. 25. [h] Triclinic form. [i] Ref. 26. [j] Tetragonal form. [k] Ref. 24. [l] P. W. G. Newman, C. L. Raston, and A. H. White, *J.C.S. Dalton*, 1973, 1332. [m] Ref. 30.

Figure 3 shows stereoscopic views of the unit cells of (I) and (II). Both crystal structures consist of discrete, well-separated molecules, a fact confirmed by the lack in either of intermolecular non-bonded distances <3·5 Å. The intramolecular non-bonded contacts in (II) are of interest since the co-ordination geometry of the copper atom is governed by steric effects, and selected distances are listed in Table 5. The methyl hydrogen atoms attached to C(4) and C(8) appear to be firmly ' locked,' and their closest non-bonded approaches to other atoms are: H(4A) · · · Cu 2·93(6), H(4C) · · · C(7) 3·04(5), H(8B) · · · Cu 2·92(7), and H(8C) · · · C(3) 2·89(8) Å.

Both unique pyrazolyl rings in (II) are planar, but the groups of atoms N(1), N(2), N(1′), N(2′), and N(3), N(4), N(3′), N(4′) deviate to some extent from planarity (see Table 4; primed atoms are related to unprimed atoms by the crystallographic two-fold axis through the molecule). The former group is the most non-planar, and the six-membered ring comprising Ga(1), Cu, N(1), N(2), N(1′), N(2′) could almost be described as having a twist conformation. The dihedral angles (24·3 and 10·4°) between the pyrazolyl ring planes and their two-fold related counterparts are indicative of the different degree of twist in the two ' halves ' of the molecule, a difference perhaps arising from packing forces within the crystals.

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