Chemistry of the Group 1B Metals. Part 16.† Crystal and Molecular Structures of [*ortho*-Phenylenebis(dimethylarsine)][tetrakis(1-pyrazolyl)-borato-N^2,$N^{2'}$]copper(I) and Bis[*ortho*-phenylenebis(dimethylarsine)]-copper(I) Hexafluorophosphate(V)

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The crystal structures of the title compounds, $[Cu\{(AsMe_2)_2C_6H_4\text{-}o\}\{(C_3H_3N_2)_4B\}]$, (1) and $[Cu\{(AsMe_2)_2C_6H_4\text{-}o\}_2][PF_6]$, (2) have been determined by single-crystal *X*-ray diffraction methods at 295 K and refined by least squares to residuals of 0.037 and 0.038 for 3 005 and 702 independent ' observed ' reflections respectively. Crystals of (1) are monoclinic, space group $P2_1/n$, with a = 12.819(4), b = 17.388(10), c = 12.042(6) Å, β = 93.22(4)°, and Z = 4. The complex is mononuclear and comprises a copper(I) species in a four-co-ordinate environment, each ligand acting as a chelate. The potential symmetry of the system is lost because of steric interactions between the ligand substituents: Cu–As, 2.370(1), 2.333(1); Cu–N, 1.987(4), 2.016(4) Å. Crystals of (2) are orthorhombic, space group *Fddd*, with a = 21.35(1), b = 20.46(1), and c = 13.262(9) Å. The cation and anion each have 222 symmetry although the latter is disordered. The copper atom of the cation is co-ordinated by the two bidentate arsine ligands, Cu–As, 2.360(1) Å, the interligand angular geometry being irregular [As–Cu–As, 113.64(5), 126.39(6)°].

IN the course of studies of the chemistry of poly(pyrazolyl)borate derivatives of copper(I) carbonyls, we synthesised the complex [Cu(pdma){B(pz)$_4$}] [pdma = o-$C_6H_4(AsMe_2)_2$; pz = $C_3H_3N_2$, 1-pyrazolyl].[1] A room-temperature ^{1}H n.m.r. spectrum of this complex indicated that all four pyrazolyl groups were magnetically equivalent, while at lower temperatures, changes in the spectra suggested that at least two fluxional processes were occurring. At −60 °C, the spectrum contained four pyrazolyl proton resonances (relative intensities 4 : 2 : 2 : 4), which was interpreted in terms of an instantaneous structure in which two pyrazolyl groups were co-ordinated to copper, and two were non-co-ordinated.[2] We now describe the crystal and molecular structures of this complex, which confirm that in the solid state the poly(pyrazolyl)borate ligand is acting as a bidentate group. For a comparison of the geometry of the Cu–pdma system, the complex [Cu(pdma)$_2$][PF$_6$] was prepared, and its structure was also determined.

EXPERIMENTAL

[Cu(pdma){B(pz)$_4$}], (1).—The preparation of this complex has been described previously;[1] a sample was recrystallised from light petroleum–diethyl ether to give well formed white crystals suitable for the *X*-ray study.

[Cu(pdma)$_2$][PF$_6$], (2).—A solution of pdma (4 cm^3 of a 4.6% solution in ethanol; 0.64 mmol) was added to [Cu(NCMe)$_4$][PF$_6$] (121 mg, 0.32 mmol) in tetrahydrofuran (thf) (15 cm^3). A white precipitate formed immediately, which was filtered off, washed with thf, and recrystallised (light petroleum–ethanol) to give *crystals* of [Cu(pdma)$_2$][PF$_6$] (2) (199 mg, 78%) (Found: C, 31.3; H, 4.1. $C_{20}H_{32}As_4CuF_6P$ requires C, 30.75; H, 4.1%).

Crystallography.—*Crystal data for* (1). $C_{22}H_{28}As_2BCuN_8$, M = 628.7, Monoclinic, space group $P2_1/n$ (C_{2h}^5, no. 14), a = 12.819(4), b = 17.388(10), c = 12.042(6) Å, β = 93.22(4)°, U = 2 680(3) Å^3, D_m = 1.55(1), Z = 4, D_c = 1.56 g cm^{-3}, $F(000)$ = 1 264. Monochromatic Mo-K_α radiation (λ = 0.710 6_9 Å), μ = 20.7 cm^{-1}. Specimen size: 0.10 × 0.20 × 0.50 mm. T = 295(1) K.

(2). $C_{20}H_{32}As_4CuF_6P$, M = 780.7, Orthorhombic, space group *Fddd* (D_{2h}^{24}, no. 70), a = 21.35(1), b = 20.46(1), c = 13.262(9) Å, U = 5 793(7) Å^3, D_m = 1.77 (1), Z = 8, D_c = 1.79 g cm^{-3}, $F(000)$ = 3 056. Radiation as above, μ = 52.7 cm^{-1}. Specimen size: ' octahedron ', axial lengths 0.27 × 0.27 × 0.20 mm. T = 295(1) K.

Structure determination. Unique data sets measured to $2\theta_{max.}$ 50° (1) and 55° (2), on a Syntex $P2_1$ four-circle diffractometer in the conventional θ—2θ scan mode, yielded 4 602 (1) and 1 682 (2) independent reflections. Of these, 3 005 (1) and 702 (2) with $I > 3\sigma(I)$ were considered observed ' and used in the structure determination and refinement after absorption correction. Refinement was by 9 × 9 block-diagonal least squares, all atoms except those of hydrogen being refined with anisotropic thermal parameters. Aromatic hydrogen-atom positional parameters were refined in (1); otherwise hydrogen-atom positions were obtained from difference maps and ' improved ' to tetrahedral and trigonal estimates. Hydrogen-atom thermal parameters were constrained at $U_H = \langle U_{ii}$ (parent C)$\rangle$ × 1.25 (aromatic), × 1.5 (methyl). Final residuals (R, R') were 0.037, 0.040 (1); 0.038, 0.044 (2), reflection weights being $[\sigma^2(F_o) + 0.000\,3(F_o)^2]^{-1}$. Computation was carried out using the ' *X*-RAY '76 ' program system,[3] implemented on a Perkin-Elmer 8/32 computer by S. R. Hall. Neutral-atom scattering factors were used, those for the non-hydrogen atoms being corrected for anomalous dispersion (f',f'').[4-6] Material deposited as Supplementary Publication No. SUP 22950 (26 pp.) § comprises tables of structure factor amplitudes, thermal parameters, hydrogen-atom geometries, and ligand planes.

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† Part 15, preceding paper.

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§ For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1980, Index issue.

Table 1

Atomic fractional cell co-ordinates of (1)

Atom	x	y	z
Cu	0.267 10(5)	0.046 41(4)	−0.041 80(5)
(*a*) Arsine ligand, section a			
C(1)	0.128 3(4)	0.065 9(3)	0.191 2(4)
C(2)	0.054 3(4)	0.087 2(3)	0.265 6(5)
H(2)	0.008(4)	0.121(3)	0.241(4)
C(3)	0.057 0(5)	0.058 8(4)	0.372 0(5)
H(3)	0.004(4)	0.071(3)	0.422(4)
C(4)	0.156 8(5)	0.217 1(3)	0.076 9(6)
H(4A)	0.106(−)	0.240(−)	0.121(−)
H(4B)	0.224(−)	0.224(−)	0.116(−)
H(4C)	0.157(−)	0.239(−)	0.005(−)
C(5)	−0.022 9(5)	0.114 2(4)	0.004 8(5)
H(5A)	−0.055(−)	0.065(−)	0.005(−)
H(5B)	−0.057(−)	0.148(−)	0.053(−)
H(5C)	−0.025(−)	0.135(−)	−0.069(−)
As	0.126 74(4)	0.108 90(3)	0.041 16(5)
(*b*) Arsine ligand, section b			
C(1)	0.206 1(4)	0.014 6(3)	0.226 1(4)
C(2)	0.209 7(4)	−0.013 7(3)	0.334 3(5)
H(2)	0.254(4)	−0.049(3)	0.353(4)
C(3)	0.132 9(5)	0.007 6(3)	0.406 3(4)
H(3)	0.128(4)	−0.011(3)	0.479(5)
C(4)	0.439 5(5)	0.005 9(4)	0.210 2(5)
H(4A)	0.445(−)	0.058(−)	0.230(−)
H(4B)	0.445(−)	−0.024(−)	0.280(−)
H(4C)	0.491(−)	−0.011(−)	0.164(−)
C(5)	0.302 4(6)	−0.129 5(4)	0.142 7(6)
H(5A)	0.318(−)	−0.146(−)	0.218(−)
H(5B)	0.233(−)	−0.149(−)	0.122(−)
H(5C)	0.351(−)	−0.146(−)	0.094(−)
As	0.311 02(4)	−0.017 90(3)	0.124 31(5)
(*c*) Tetrapyrazolylborate ligand			
B	0.296 3(5)	0.119 9(3)	−0.285 7(5)
(*i*) Pyrazole a			
N(1)	0.293 2(3)	0.031 0(2)	−0.279 2(3)
N(2)	0.263 7(3)	−0.007 3(2)	−0.187 6(3)
C(3)	0.259 7(4)	−0.081 1(3)	−0.215 8(4)
H(3)	0.243(4)	−0.112(3)	−0.162(4)
C(4)	0.285 0(5)	−0.091 5(3)	−0.323 6(5)
H(4)	0.282(4)	−0.135(3)	−0.368(4)
C(5)	0.306 5(4)	−0.020 6(3)	−0.361 3(4)
H(5)	0.325(4)	−0.002(3)	−0.428(4)
(*ii*) Pyrazole b			
N(1)	0.367 3(3)	0.155 1(2)	−0.192 0(3)
N(2)	0.364 4(3)	0.131 0(2)	−0.085 5(3)
C(3)	0.423 3(4)	0.181 2(3)	−0.025 4(4)
H(3)	0.425(4)	0.183(3)	0.050(4)
C(4)	0.462 5(4)	0.237 0(3)	−0.091 1(5)
H(4)	0.511(4)	0.276(3)	−0.065(4)
C(5)	0.426 5(4)	0.218 7(3)	−0.195 5(5)
H(5)	0.435(4)	0.245(3)	−0.263(4)
(*iii*) Pyrazole c			
N(1)	0.185 5(3)	0.150 5(2)	−0.278 3(3)
N(2)	0.170 0(3)	0.226 3(2)	−0.259 3(4)
C(3)	0.067 7(5)	0.235 4(3)	−0.270 7(5)
H(3)	0.049(4)	0.279(3)	−0.255(4)
C(4)	0.016 6(4)	0.168 1(3)	−0.296 6(5)
H(4)	−0.048(4)	0.162(3)	−0.302(4)
C(5)	0.093 7(4)	0.115 2(3)	−0.300 4(4)
H(5)	0.088(4)	0.062(3)	−0.317(5)
(*iv*) Pyrazole d			
N(1)	0.337 4(3	0.143 6(2)	−0.397 9(3)
N(2)	0.436 8(4)	0.125 0(3)	−0.423 7(4)
C(3)	0.443 3(5)	0.146 5(4)	−0.527 8(5)
H(3)	0.506(4)	0.142(3)	−0.565(4)
C(4)	0.353 1(5)	0.178 6(4)	−0.569 3(5)
H(4)	0.336(4)	0.197(3)	−0.647(4)
C(5)	0.287 1(5)	0.175 3(3)	−0.486 7(5)
H(5)	0.220(4)	0.187(3)	−0.480(5)

Fractional atomic co-ordinates are given in Tables 1 and 2 for (1) and (2) respectively. Hydrogen-atom numbering follows that of the parent carbon atom. Methyl hydrogen atoms are suffixed A, B, C for distinguishing purposes.

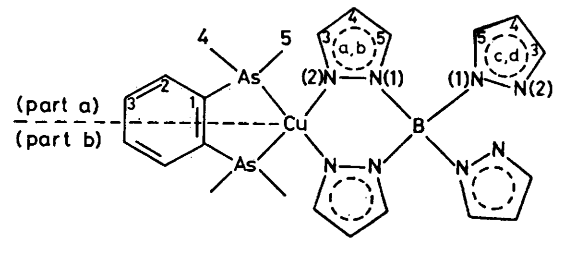
Table 2

Atomic fractional cell co-ordinates of (2)

Atom	x	y	z
Cu	0.125 00(−)	0.125 00(−)	0.625 00(−)
(*a*) Arsine ligand			
C(1)	0.149 7(4)	−0.039 3(4)	0.591 7(7)
C(2)	0.173 5(4)	−0.098 3(5)	0.557 0(7)
H(2)	0.208(−)	−0.099(−)	0.511(−)
C(3)	0.149 3(4)	−0.156 6(4)	0.590 9(7)
H(3)	0.168(−)	−0.196(−)	0.570(−)
C(4)	0.271 8(4)	0.033 0(4)	0.587 7(7)
H(4A)	0.276(−)	0.030(−)	0.661(−)
H(4B)	0.293(−)	−0.002(−)	0.558(−)
H(4C)	0.290(−)	0.075(−)	0.567(−)
C(5)	0.193 7(5)	0.027 2(6)	0.400 2(8)
H(5A)	0.221(−)	−0.006(−)	0.384(−)
H(5B)	0.154(−)	0.021(−)	0.368(−)
H(5C)	0.211(−)	0.070(−)	0.375(−)
As	0.185 49(4)	0.043 68(4)	0.544 75(8)
(*b*) Anion			
P	0.125 00(−)	0.125 00(−)	0.125 00(−)
F(1) *	0.156(3)	0.062(2)	0.098(6)
F(2) *	0.067(2)	0.079(2)	0.085(4)
F(3) *	0.125(4)	0.098(3)	0.227(2)
F(4) *	0.080(2)	0.100(4)	0.193(6)

* Populations: 0.38(−).

In (2) the PF_6 species was found to be ' disordered '; fluorine fragment populations were assessed from a difference map to be approximately equal and were refined as such. The possibility that the true space group was of lower symmetry was considered but not explored further as it was believed that the likelihood of successful refinement based on distinct PF_6 groups was remote.



RESULTS AND DISCUSSION

[Cu(pdma){B(pz)$_4$}], (1).—The structure determination shows the unit-cell contents to be comprised of mononuclear [Cu(pdma){B(pz)$_4$}] species with no unusually short intermolecular contacts (Figure 1). As anticipated from the results of the ^{1}H n.m.r. study, the copper atom is co-ordinated by the two arsenic atoms of the diarsine ligand and by only two of the four available pyrazolyl nitrogen atoms of the [B(pz)$_4$]$^-$ ligand.

Co-ordination about the copper atom. The four donor ligands are approximately tetrahedrally disposed about the copper atom (Table 3 and Figure 3). Angles enclosed by the chelate ligands at the copper atom are As–Cu–As, 90.61(4)° and N–Cu–N, 95.5(2)°; in [Cu(CO){BH(pz)$_3$}] where the poly(pyrazolyl)borate ligand is tridentate, N–Cu–N vary between 90.4(1) and 92.4(2)°.[7]

In both complexes, these angles are well below the tetrahedral angle of 109.5° and result from the requirements for normal Cu–N distances and the constraints imposed by the tetrakis(pyrazolyl)borate ligand. Consequently, the N–Cu–As angles are greater than the tetrahedral angle generally, although there are very wide variations, the lower limit in fact lying beneath the tetrahedral value [range 105.7(1) to 127.5(1)°]. The Cu–N distances [1.987(4), 2.016(4) Å] are slightly less than those observed in [Cu(CO){BH(pz)$_3$}][2.039(4), 2.059(3) Å] and somewhat longer than those observed to the non-bridging pyrazolyl groups in [Cu$_2${BH(pz)$_3$}$_2$][1.946(2), 1.948(2) Å].[8] Although the copper atom has potential D_{2d} symmetry it may be that the above departures from this ideal could be consequent upon steric interactions within and between ligands and these are discussed below.

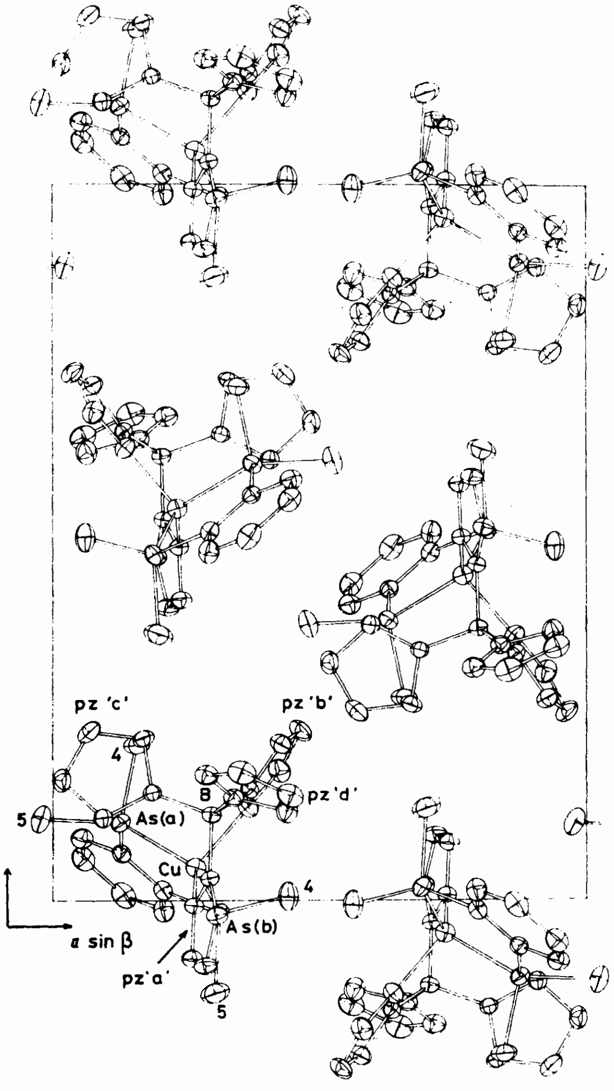


FIGURE 1 Unit-cell contents of (1), projected down *c*. Non-hydrogen atoms only are shown with 20% thermal ellipsoids

Geometry of the o-C$_6$H$_4$(AsMe$_2$)$_2$ *ligand.* Of the many complexes containing this ligand which have been studied by *X*-ray diffraction methods, relatively few contain only one pdma ligand bonded to a metal atom. Further, no previous example of a copper(I)–pdma complex has been structurally characterised, although the related binuclear complex [{Cu(μ-I)[C$_6$H$_4$(NMe$_2$)(AsMe$_2$)-*o*]}$_2$] was described in 1971.[9] In this complex, the ligand-enclosed As–Cu–N angle is 83.3(8)°, with a Cu–As distance of 2.334(7) Å, not significantly different from one of the Cu–As bonds in the present complex, which are 2.333(1) and 2.370(1) Å. The geometry of the ligand in the present case (Table 4) has no features of note, distances and angles being similar to those found in other studies, those of the peripheral atoms being apparently somewhat affected by thermal motion. The enclosed angles at the arsenic atoms are 104.2(1) and 104.9(1)°, somewhat larger than those of 95(1)° found in the As–N chelate complex mentioned above, but expected on the basis of the larger bite of the pdma ligand.

TABLE 3

Copper and boron atom environments for (1)

(*a*) Distances (Å)

Cu–As(a)	2.370(1)	B–N(a1)	1.548(7)
Cu–As(b)	2.333(1)	B–N(b1)	1.537(7)
Cu–N(a1)	1.987(4)	B–N(c1)	1.524(7)
Cu–N(b1)	2.016(4)	B–N(d1)	1.534(7)

(*b*) Angles (°)

As(a)–Cu–As(b)	90.61(4)	N(a1)–B–N(b1)	112.1(4)
As(a)–Cu–N(a2)	127.5(1)	N(a1)–B–N(c1)	108.6(4)
As(a)–Cu–N(b2)	105.7(1)	N(a1)–B–N(d1)	108.9(4)
As(b)–Cu–N(a2)	121.6(1)	N(b1)–B–N(c1)	109.5(4)
As(b)–Cu–N(b2)	116.8(1)	N(b1)–B–N(d1)	108.7(4)
N(a2)–Cu–N(b2)	95.5(2)	N(c1)–B–N(d1)	109.0(4)

TABLE 4

Arsine ligand non-hydrogen atom geometry for (1) *

	Section a	Section b
(*a*) Distances (Å)		
As–C(1)	1.955(5)	1.953(5)
As–C(4)	1.963(6)	1.940(6)
As–C(5)	1.946(6)	1.956(7)
C(1)–C(1′)	1.384(7)	
C(1)–C(2)	1.392(8)	1.392(7)
C(2)–C(3)	1.371(8)	1.381(8)
C(3)–C(3′)	1.366(9)	
(*b*) Angles (°)		
C(1)–As–C(4)	99.9(2)	101.4(2)
C(1)–As–C(5)	100.7(2)	99.8(3)
C(1)–As–Cu	104.2(1)	104.9(1)
C(4)–As–Cu	112.8(2)	120.8(2)
C(5)–As–Cu	133.6(2)	124.1(2)
C(4)–As–C(5)	100.5(3)	101.8(3)
As–C(1)–C(1′)	119.8(4)	120.4(4)
As–C(1)–C(2)	121.4(4)	120.6(4)
C(1′)–C(1)–C(2)	118.8(5)	119.0(5)
C(1)–C(2)–C(3)	121.6(5)	121.2(5)
C(2)–C(3)–C(3′)	119.9(5)	119.5(5)

* Primed atoms lie in the other half of the ligand.

While the ligand itself has normal distances and angles in its relationship to the copper atom, a number of distortions from regularity are observed, notably to be found in the angles subtended at the arsenic atom by the copper atom and the methyl groups, these ranging between 112.8(2) and 133.6(2)°. A least-squares plane has been calculated through the C_6As_2 skeleton of the ligand. Atom deviations are [C(a1—3,b1—3)As(a,b)]: −0.01, −0.01, 0.00, 0.00, 0.02, 0.00, 0.02, −0.01 Å (σ, 0.01 Å). For the non-defining atoms, we find the copper atom lying −0.066 Å out of the plane, while the methyl carbon atom deviations are [C(a4,5),C(b4,5)]: 1.79, −1.13, 1.54, −1.48 Å, indicative, as the angles above confirm, of a considerable asymmetry in the methyl disposition about As(a).

Geometry of the $B(pz)_4$ *ligand.* Co-ordination about the boron atom is very close to regular tetrahedral. Within the pyrazole groups interatomic distances and angles are generally mundane and show no differences, other than the trivial, between co-ordinated and unco-ordinated pyrazole rings (Table 5). Interestingly, however, a distinction *can* be found between the two halves of each ring corresponding to the boron-bonded and -non-bonded nitrogen atom, irrespective of interaction or otherwise of the pyrazole with the copper. Thus *all* C(3)–C(4) distances are greater than *all* C(4)–C(5) distances, and a similar disparity can be observed in N(1)–C(5) compared with N(2)–C(3) at a lower level; the differences are small, and the effects of a lack of librational correction uncertain, but a corresponding disparity can be asserted much more confidently in regard to the N(2)–C(3)–C(4) angle, relative to N(1)–C(5)–C(4), the former ranging over 111.3(5)—112.5(5)° and the latter 108.4(5)—109.3(5)°. The individual pyrazole rings show substantial deviations from planarity and coplanarity with the boron; for planes calculated through each of the BN_2C_3 moieties, σ values respectively for rings a, b, c, d are 0.04, 0.05, 0.04, 0.03 Å. Rings a, b, which are co-ordinated to the copper atom, are not

TABLE 5

Pyrazole non-hydrogen geometries for (1)

	Ring a	Ring b	Ring c	Ring d
(*a*) Distances (Å)				
N(1)–N(2)	1.361(5)	1.351(6)	1.354(6)	1.366(6)
N(1)–C(5)	1.354(6)	1.343(7)	1.341(6)	1.337(7)
N(2)–C(3)	1.329(6)	1.341(7)	1.320(7)	1.315(8)
C(3)–C(4)	1.367(8)	1.366(8)	1.369(8)	1.354(9)
C(4)–C(5)	1.347(7)	1.352(8)	1.351(8)	1.343(9)
(*b*) Angles (°)				
B–N(1)–N(2)	122.7(4)	121.8(4)	119.8(4)	120.5(4)
B–N(1)–C(5)	128.4(4)	128.1(4)	129.7(4)	129.9(5)
N(2)–N(1)–C(5)	108.6(4)	109.3(4)	110.1(4)	109.2(4)
Cu–N(2)–N(1)	119.5(3)	121.6(3)		
Cu–N(2)–C(3)	132.8(3)	132.3(4)		
N(1)–N(2)–C(3)	105.9(4)	105.3(4)	104.7(4)	105.0(5)
N(2)–C(3)–C(4)	111.3(5)	111.5(5)	112.5(5)	111.8(6)
C(3)–C(4)–C(5)	105.2(5)	104.6(5)	104.3(5)	105.6(5)
C(4)–C(5)–N(1)	109.0(4)	109.3(5)	108.5(5)	108.4(5)

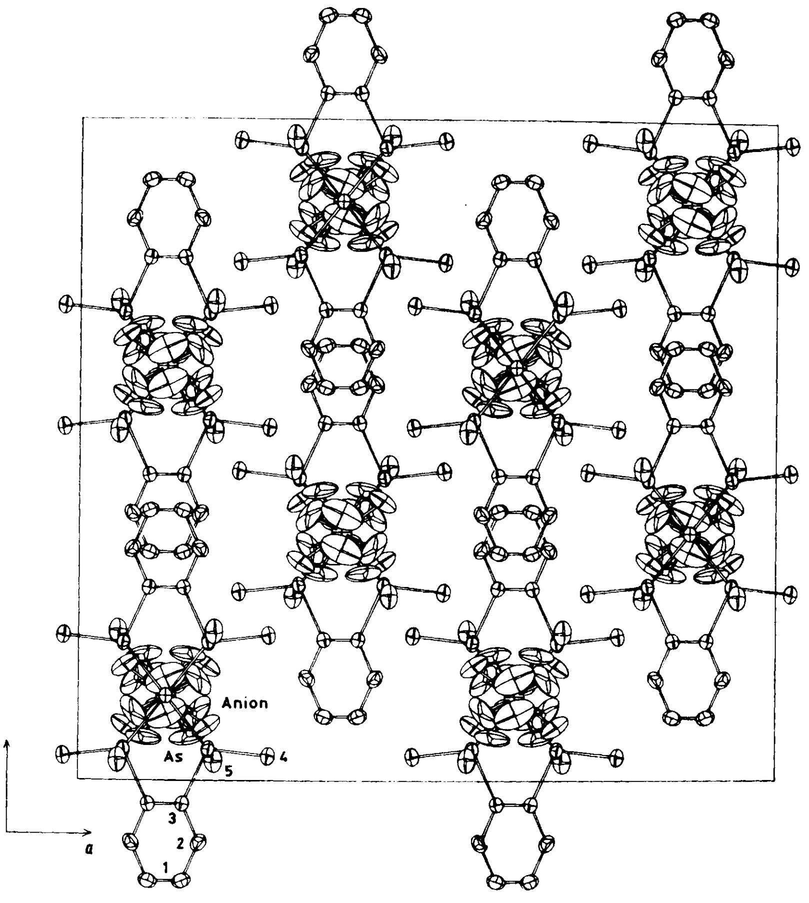


FIGURE 2 Unit-cell contents of (2), projected down *c*, as for Figure 1

coplanar with each other, having an interplanar dihedral angle of 41.6°. The deviation of the copper atom from pyrazolyl planes a, b is 0.44, 0.20 Å respectively. Since there appear to be *no* H · · · H contacts <2.8 Å between the methyl hydrogen atoms of the arsine ligand and the H(2a,b) of the pyrazolyl co-ordinating ligands, it appears that the asymmetry observed in the chelation of the copper by the arsine ligand is not influenced by the proximity of the bulky tetrapyrazolylborate ligand; neither, for that matter, is the angular asymmetry about the arsenic atoms. The origin of all of the distortions from regularity concerned with the arsine ligand must therefore be either internal or a consequence of packing forces; in regard to the latter, there are no notably short intermolecular contacts, and their effect, as is usually the case, must remain uncertain. Within the tetrapyrazolylborate ligand, we note that there are no inter-ring H · · · H contacts <3.0 Å. There are a number of significant H · · · N contacts, all involving H(5) and lying close to the van der Waals H · · · N estimate of *ca.* 2.7 Å (Table 6) and the endocyclic angular discrepancy noted above at C(3) and C(5) of each ring may have its origin in these interactions. In addition we note that the exocyclic angles at the hydrogen atom H(5) in each case range over 129(3)—135(4)° for C(4)-C(5)-H(5), while N(1)-C(5)-H(5) are 116(4)—123(3)°. In view of this and the fact that the endocyclic angle at C(5) is *less* than that

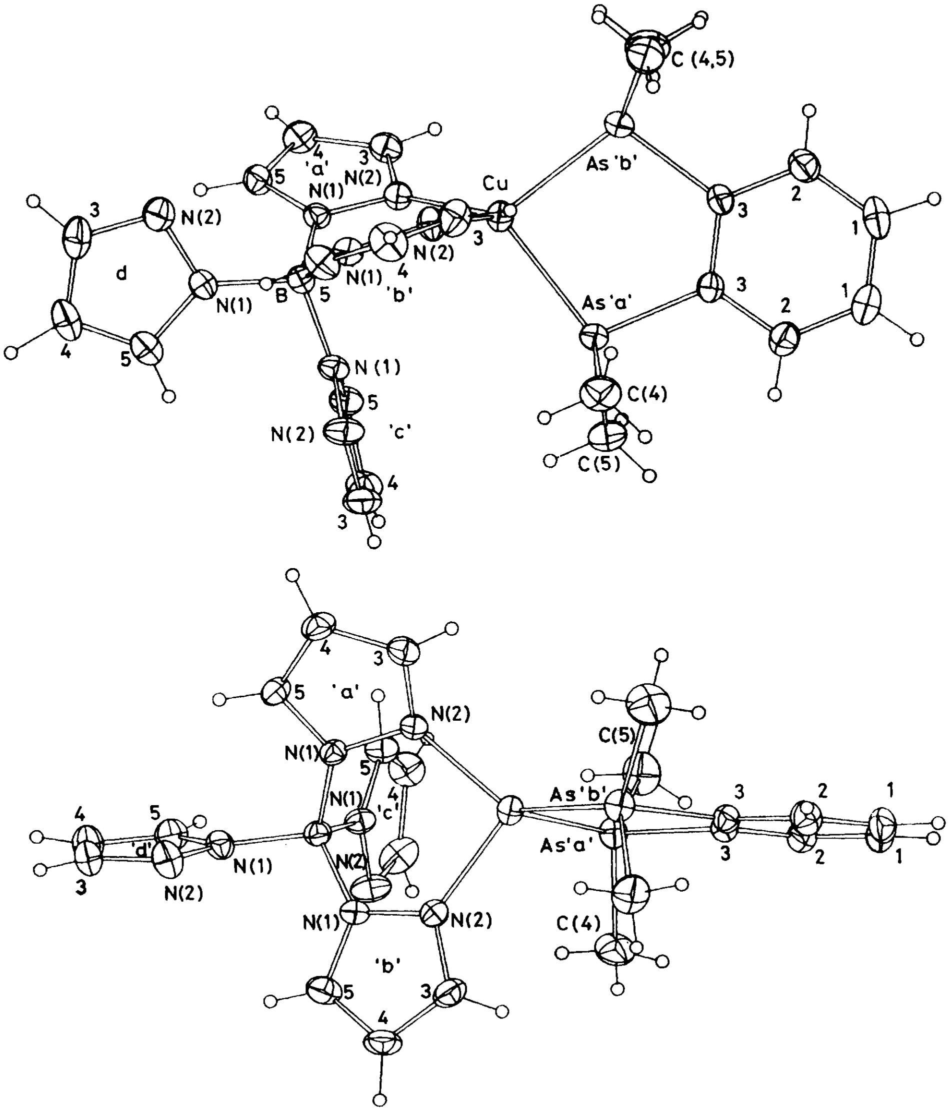


FIGURE 3 A molecule of (1) projected normal to the plane of the CuN_2 group. Hydrogen atoms are shown with a radius of 0.1 Å

TABLE 6

Contacts between the component parts of the molecule of (1) (H · · · N, ≤2.7 Å; H · · · C, <3.0 Å)

Atoms	Distance/ Å	Atoms	Distance/ Å
H(a5) · · · N(d1)	2.56(5)	H(c5) · · · N(a1)	2.70(5)
H(a5) · · · N(d2)	2.64(5)	H(c5) · · · N(a2)	2.93(5)
H(b5) · · · N(d1)	2.66(5)	H(d5) · · · N(c1)	2.57(6)
H(b5) · · · N(d2)	2.84(5)	H(d5) · · · N(c2)	2.85(6)

at C(3), it seems reasonable to conclude that the N • • • H(5) interactions may be attractive rather than repulsive. However, in opposition to this view we note that for *all* rings the B–N(1)–N(2) angle [range 119.8(4)—122.7(4)°] is substantially less than the B–N(1)–C(5) angle [range 128.1(4)—129.9(5)°].

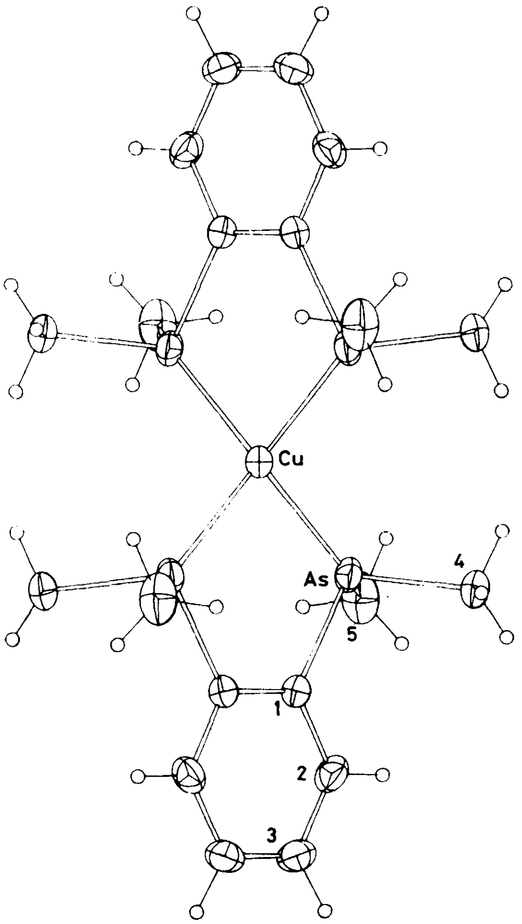


FIGURE 4 The cation of (2) projected down *c*. Hydrogen atoms are shown with a radius of 0.1 Å

[Cu(pdma)$_2$)][PF$_6$], (2).—The structure determination shows the unit-cell contents to be comprised of [Cu(pdma)$_2$]$^+$ cations and [PF$_6$]$^-$ anions, both located about sites of 222 symmetry, the [PF$_6$]$^-$ ion being ' disordered ' (Figure 2). In the cation, the copper atom is chelated by two pdma ligands (Figure 4). The Cu–As distance of 2.360(1) Å lies in between the two values found in (1) (Table 7). The CuAs$_4$ interligand angular geometry is surprisingly irregular and well distorted from tetrahedral or *mm* symmetry, the two independent As–Cu–As angles being 113.64(5) and 126.39(6)°. This appears to be a consequence of packing forces, there being no intramolecular, interligand H • • • H contacts <2.5 Å. Calculation of a least-squares plane through the C$_6$ skeleton of the aromatic ring shows no deviation >0.01 Å (σ, 0.007 Å); δ As is 0.04 Å and δ Cu, 0.00 Å. The two methyl groups are unsymmetrically disposed with respect to the plane [δC(4), 1.68; δC(5), −1.29 Å].

TABLE 7

Cation non-hydrogen geometry for (2)

(*a*) Distances (Å)

Cu–As	2.360(1)	C(1)–C(1^I)	1.38(1)
As–C(1)	1.964(8)	C(1)–C(2)	1.39(1)
As–C(4)	1.940(8)	C(2)–C(3)	1.37(1)
As–C(5)	1.955(10)	C(3)–C(3^I)	1.38(1)

(*b*) Angles (°)

As–Cu–As^{II}	113.64(5)	C(5)–As–Cu	127.8(3)
As–Cu–As^I	90.33(6)	C(4)–As–C(5)	100.6(4)
As–Cu–As^{III}	126.39(6)	As–C(1)–C(1^I)	120.1(6)
C(1)–As–C(4)	100.3(3)	As–C(1)–C(2)	120.3(6)
C(1)–As–C(5)	101.3(4)	C(1^I)–C(1)–C(2)	119.6(7)
C(1)–As–Cu	104.7(2)	C(1)–C(2)–C(3)	120.6(9)
C(4)–As–Cu	117.8(3)	C(2)–C(3)–C(3^I)	119.9(8)

Transformations of the asymmetric unit: I ($\frac{1}{4} - x, y, \frac{5}{4} - z$); II ($x, \frac{1}{4} - y, \frac{5}{4} - z$); III ($\frac{1}{4} - x, \frac{1}{4} - y, z$).

We gratefully acknowledge grants from the Australian Research Grants Committee in support of this work.

[0/1083 *Received*, 9*th July*, 1980]

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