Inorganica Chimica Acta, 83 (1984) 177–189

Crystal Structures of α- and β-(1,10-Phenanthroline)tetrahydroborato-(triphenylphosphine)copper(I) and (2,9-Dimethyl-4,7-diphenyl-1,10-phenanthroline)tetrahydroboratocopper(I)*

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Received July 9, 1983

Copper(I) is five coordinate in (1,10-phenanthroline)tetrahydroborato(triphenylphosphine)copper(I). This compound crystallises from either toluene as the yellow, α-form, a = *16.247(8),* b = *9.750(7),* c = *9.322(5)* Å, α = *62.92(4),* β = *84.77(4),* γ = *84.34(5)°, triclinic* P$\bar{1}$, Z = *2, or from a xylene/methylene chloride mixture as the red β-form, X-ray cell,* a = *13.675(11),* b = *10.115(8),* c = *9.700(7)* Å, α = *95.22(6),* β = *96.22(6),* γ = *101.02(6)°; neutron cell, as the tetradeuteroborate,* a = *13.703(1),* b = *10.096(8),* c = *9.74(1)* Å, α = *95.23(9),* β = *96.51(8),* γ = *101.04(2)°, triclinic,* P$\bar{1}$, Z = *2. For both forms, unidentate triphenylphosphine, bidentate 1,10-phenanthroline and unsymmetrical bidentate* BH_4^- *completes the copper(I) coordination but there are subtle differences between the two. When the ligand 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline,* dmdp, *replaces 1,10-phenanthroline, the compound obtained is four coordinate with no* tpp *in the crystal. [C(*dmdp*)BH_4] is monoclinic,* Cc, a = *14.522(4),* b = *20.07(2),* c = *7.718(2)* Å, β = *106.17(2)°,* Z = *4.*

Introduction

In order to verify the presence of five coordinated copper(I) for the yellow α-(1,10-phenanthroline)-tetrahydroborato(triphenylphosphine)copper(I), [Cu(*phen*)(*tpp*)BH_4], (*tpp* = triphenylphosphine, *phen* = 1,10-phenanthroline), (*II*), [2], X-ray and neutron data were collected for the borohydride and borodeuteride, respectively. However, the red crystals, the β-form, (*III*), grown from xylene/methylene chloride, had different unit cell dimensions from α. Because of these problems, α was refined using recollected X-ray data. Another member of the series, [Cu(*dmdp*)BH_4], (*IV*), (where *dmdp* = 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline), was also investigated.

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*Stereochemistry of Rigid Chelate-Metal Complexes. *(VIII)*. Part *(VII)*: (2,2′-Bipyridine)chloro(triphenylphosphine)copper(I) Hydrate, *(I)* [1].

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0020-1693/84/$3.00

TABLE I. Experimental Data.[a]

	Cu(*phen*)(*tpp*)BH_4]		[Cu(*phen*)(*tpp*)BD_4]	[Cu(*dmdp*)BH_4
	α-yellow	β-red	β-red	
A. *Crystal Parameters*				
Formula	$C_{30}H_{27}BCuN_2P$	$C_{30}H_{27}BCuN_2P$	$C_{30}H_{23}BCuD_4N_2P$	$C_{26}H_{24}BCuN_2$
Space Group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	*Cc*
a (Å)	16.247(8)	13.675(11)	13.703(1)	14.522(4)
b	9.750(7)	10.115(8)	10.096(8)	20.07(2)
c	9.322(5)	9.700(7)	9.74(1)	7.718(2)
α (degrees)	62.92(4)	95.22(6)	95.23(9)	90
β	84.77(4)	96.22(6)	96.51(8)	106.17(2)
γ	84.34(5)	101.02(6)	101.04(2)	90
V (Å^3)	1307(1)	1301(2)	1306(1)	2168(2)
Z	2	2	2	4
Mol. Wt.	520.9	520.9	524.9	438.5
ρ(Calcd) (g cm^{-3})	1.32	1.33	1.33	1.34
ρ(Found) (g cm^{-3})	1.31	1.32	1.33	1.33
F(000)	540	540	540	912
B. *Measurement of Data*				
Diffractometer	Syntex $P2_1$	Syntex $P2_1$	AAEC modified Stoe	Syntex $P2_1$
radiation	MoKα	MoKα	neutron	MoKα
λ (Å)	0.7107	0.7107	1.238	0.7107
Reflections Measured:				
2θ Maximum (°)	50	50	71	50
Scanning mode	$2\theta-\omega$	$2\theta-\omega$	$2\theta-\omega$	$2\theta-\omega$
Reflections Collected:				
Total	4075	3425	1895	1420
Unique	2929	2713	1320	1359
$I > n\sigma(I)$ where n =	2.5	2.5	2.0	1.5
μ (cm^{-1})	0.90	0.90	2.59	0.35
Corrections applied			absorption	
Crystal size (mm)	0.25 × 0.2 × 0.2	0.24 × 0.21 × 0.2	5.50 × 1.8 × 1.7	0.2 × 0.1 × 0.1
$R = [\Sigma\lVert Fo\rvert - \lvert Fc\rVert / -\Sigma\lvert Fo\rvert]$	0.08	0.06	0.12	0.06

$R_w = [(\Sigma w\|\|Fo\| - \|Fc\|\|^2 - / \Sigma w\|Fo\|^2)^{1/2}]$		0.09	0.06		0.06
maximum background in final difference map (eÅ^{-3})		0.30	0.23	0.03	0.18
Weighting scheme					
$A/(\sigma^2 F + BF^2)$	A	4.04	4.65	unit	1.44
	B	1×10^{-4}	2×10^{-4}	weights	4×10^{-4}

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[a] For neutron determination: the scattering lengths used were C, 0.665; H, −0.372; B, 0.060; N, 0.94; P, 0.51; Cu, 0.76; D, 0.621 cm^{-1}.

Experimental

Synthesis

[Cu(*phen*)(*tpp*)BH_4] was prepared by the modification of the method in [3] as described in [2]. Compounds (*II*) and (*III*) were recrystallised from toluene and xylene/methylene chloride, respectively.

Compound (*IV*) was prepared similarly to Cu(*dmp*)BH_4, (*V*), (*dmp* = 2,9-dimethyl-1,10-phenanthroline), [4], by reacting anhydrous *dmdp* dissolved in dry toluene with a dry toluene solution of Cu(*tpp*)$_2BH_4$, (*VI*). The amber crystals were formed from a dry methylene chloride/xylene solution when the mixed solvent was evaporated by a slow stream of dry nitrogen. *Anal.* Found: C, 70.9; H, 5.6; N, 6.18%. Calcd. For $C_{26}H_{24}BCu$: C, 71.2; H, 5.52; N, 6.39%.

For infrared spectra, solid samples were prepared in nujol and HCBD as mulls between CsI plates and the spectra were determined using a Perkin-Elmer 225 infrared spectrometer. Solution spectra of samples in dry methylene chloride and toluene were recorded in matched compensated cells fitted with KBr windows.

Crystal Data

Details of cell constants and data acquisition are given in Table I. Neutron data were collected on the 2 TAN A facility of the A.A.E.C.'s HIFAR reactor at Lucas Heights, N.S.W., Australia.

Intensity Data, Structure Determination and Refinement

The redetermination and refinement of α (*II*), based on a previous determination, [2], produced a marginally improved result. Although twice the number of reflections were used, the standard deviations were only reduced by half. Difficulties were experienced in locating the hydrogen atoms on the peripheral phenyl rings, where the carbons have reasonably high thermal parameters, and in locating the hydrogens in the BH_4^- group.

The structure of (*III*) was solved by placing one copper atom at the origin in space group *P1* which gave two related molecules. On shifting the origin, the asymmetric molecule in $P\bar{1}$ was located, then the structure was refined using SHELX, [5]. The neutron structure was refined using the X-ray coordinates for (*III*), with the hydrogen atoms being located from the first difference-Fourier synthesis.

The structure of (*IV*) was solved by symbolic addition in the space group *C2/c*. This gave two different but related molecules. An origin shift was applied to give a unique set of coordinates. The structure was refined in *Cc* using full matrix least squares anisotropic refinement on all non-hydrogen atoms, except for boron and the 4,7-diphenyl carbon atoms which were refined isotropically. The selection of the noncentrosymmetric space group *Cc* was

TABLE II. Atomic Coordinates $\times 10^4$.

Atom	Cu(*phen*)(*tpp*)BH$_4$]						[Cu(*phen*)(*tpp*)BD$_4$]		
	α-Yellow			β-Red			β-Red		
	x/a	*y/b*	*z/c*	*x/a*	*y/b*	*z/c*	*x/a*	*y/b*	*z/c*
Cu	1544(1)	2100(1)	1767(1)	2356(1)	795(1)	591(1)	2347(8)	809(11)	575(12)
P	2833(1)	2600(2)	1812(2)	2622(1)	1525(2)	2862(2)	2635(10)	1529(14)	2871(17)
C(21)	3036(5)	2976(9)	3489(9)	2003(4)	475(6)	4064(6)	1995(9)	458(12)	4090(15)
C(22)	2751(6)	1921(11)	5014(11)	1156(5)	−488(6)	3556(6)	1126(10)	−478(13)	3558(20)
C(23)	2880(7)	2214(12)	6344(13)	641(5)	−1311(7)	4449(7)	634(12)	−13(16)	4435(19)
C(24)	3252(6)	3430(12)	6151(12)	996(5)	−1150(7)	5839(7)	1007(11)	−118(15)	5866(19)
C(25)	3528(7)	4449(12)	4698(13)	1841(5)	−207(7)	6368(2)	1847(11)	−202(15)	6379(21)
C(26)	3430(6)	4231(11)	3320(12)	2347(5)	609(6)	5497(6)	2359(11)	638(15)	5507(18)
C(31)	3213(5)	4257(9)	52(9)	3952(4)	1803(6)	3550(6)	3943(8)	1802(10)	3546(13)
C(32)	2636(6)	5443(11)	−696(12)	4465(5)	837(7)	3086(7)	4450(11)	803(16)	3076(18)
C(33)	2868(7)	6843(13)	−2093(14)	5515(6)	960(8)	3520(8)	5482(11)	895(16)	3550(18)
C(34)	3674(7)	6922(13)	−2688(14)	5986(6)	2058(8)	4478(8)	6009(12)	2008(14)	4507(17)
C(35)	4227(7)	5719(13)	−1967(13)	5492(5)	3023(7)	4924(7)	5481(91)	3016(15)	4928(17)
C(36)	4008(5)	4392(10)	−584(10)	4464(5)	2906(6)	4473(6)	4471(9)	2914(13)	4470(15)
C(41)	3603(5)	1044(9)	1999(9)	2281(4)	3170(6)	3253(6)	2309(9)	3199(12)	3239(15)
C(42)	4303(6)	639(11)	2904(11)	1671(5)	3436(7)	4247(7)	1661(12)	3438(17)	4234(19)
C(43)	4846(7)	−603(12)	3006(13)	1375(6)	4706(8)	4362(8)	1364(12)	4737(16)	4384(20)
C(44)	4722(7)	−1396(13)	2205(13)	1680(6)	5628(8)	3507(8)	1673(12)	5675(18)	3529(18)
C(45)	4035(7)	−994(12)	1246(13)	2276(5)	5407(7)	2547(7)	2314(11)	5424(16)	2517(19)
C(46)	3478(5)	204(10)	1169(10)	2590(5)	4154(6)	2411(6)	2618(9)	4177(12)	2388(16)
N(1)	1186(4)	2163(7)	−387(7)	3518(4)	1879(6)	−441(6)	3506(6)	1906(10)	−452(10)
C(2)	984(5)	3376(10)	−1737(10)	4459(6)	1742(8)	−423(8)	4432(12)	1747(16)	−436(18)
C(3)	717(6)	3261(11)	−3087(12)	5185(7)	2619(9)	−964(10)	5217(13)	2620(18)	−936(21)
C(4)	662(6)	1861(11)	−2994(12)	4930(7)	3675(9)	−1518(9)	4953(13)	3686(18)	−1531(20)
C(5)	802(6)	−1015(11)	−1326(12)	3610(7)	5044(9)	−2119(9)	3644(14)	5062(19)	−2090(22)
C(6)	984(7)	−2209(13)	17(14)	2700(6)	5205(8)	−2108(9)	2684(13)	5228(18)	−2104(20)
C(7)	1469(7)	−3303(13)	2880(14)	949(6)	4372(8)	−1476(9)	940(12)	4418(16)	−1539(18)
C(8)	1660(7)	−3041(13)	4082(14)	330(6)	3473(8)	−949(8)	361(10)	3460(14)	−918(16)
C(9)	1645(7)	−1488(12)	3833(13)	674(6)	2333(7)	−425(7)	674(10)	2295(13)	−432(15)
N(10)	1487(4)	−311(7)	2439(8)	1601(4)	2151(5)	−470(5)	1592(6)	2142(9)	−46(9)
C(11)	1307(5)	−553(9)	1202(9)	2234(5)	3105(6)	−1036(6)	2233(9)	3092(12)	−1028(14)
C(12)	1254(6)	−2077(12)	1334(12)	1936(5)	4243(7)	−1553(7)	1942(10)	4233(14)	−1547(17)
C(13)	858(5)	544(10)	−1591(11)	3946(5)	3914(7)	−1583(7)	3957(12)	3927(16)	−1569(19)
C(14)	1118(5)	759(9)	−303(9)	3244(5)	2942(6)	−1034(6)	3234(9)	2931(13)	−1023(15)
B	481(5)	3202(11)	2730(12)	2130(7)	−1517(8)	−66(10)	2153(16)	−1478(22)	−47(26)
D(1)							1536(14)	−733(19)	10(21)
D(2)							2973(19)	−859(25)	57(27)
D(3)							2128(22)	−2148(31)	920(34)
D(4)							1851(24)	−2190(34)	−1102(37)
H(2)							4590(23)	745(32)	114(36)
H(3)							5929(28)	2503(38)	9001(41)
H(4)							5513(3)	4319(42)	8120(46)
H(5)							4139(26)	5728(35)	7490(39)
H(6)							2453(32)	6175(44)	7583(47)
H(7)							715(25)	5200(33)	8226(37)
H(8)							499(18)	6485(24)	876(29)
H(9)							160(2)	1539(35)	127(39)

[Cu(*dmdp*)BH$_4$]

Atom	*x/a*	*y/b*	*z/c*
Cu	−180(0)	966(1)	2228(0)
Ni(1)	1214(8)	985(6)	3669(14)

(continued on facing page)

TABLE II. *(continued)*

Atom	*x/a*	*y/b*	*z/c*
N(10)	45(7)	−50(5)	2355(19)
C(2)	1774(10)	1508(6)	4205(19)
C(3)	2740(9)	1434(6)	5264(16)
C(4)	3116(9)	794(6)	5808(17)
C(5)	2789(9)	−414(6)	5741(19)
C(6)	2177(9)	−944(6)	5092(16)
C(7)	616(11)	−1376(6)	3064(22)
C(8)	−257(13)	−1202(6)	1999(22)
C(9)	−565(10)	551(8)	1706(20)
C(11)	1565(8)	346(6)	4149(15)
C(12)	2526(9)	218(6)	5274(16)
C(13)	1271(9)	−859(6)	3901(19)
C(14)	964(11)	−210(7)	3453(21)
C(21)	1382(12)	2184(7)	3580(22)
C(91)	−1507(13)	−356(9)	524(27)
C(41)	4130(10)	736(7)	6846(20)
C(42)	4761(10)	310(6)	6447(17)
C(43)	5734(11)	316(8)	7376(22)
C(44)	6070(12)	780(8)	8790(23)
C(45)	5454(12)	1209(8)	9242(22)
C(46)	4467(10)	1196(7)	8268(20)
C(71)	849(9)	−2077(7)	3448(19)
C(72)	1732(10)	−2367(7)	3416(19)
C(73)	1898(12)	−3034(8)	3746(22)
C(74)	1230(10)	−3445(7)	4133(20)
C(75)	380(11)	−3196(8)	4213(21)
C(76)	148(10)	−2499(7)	3825(20)
B	−1362(9)	1610(6)	1260(17)

TABLE IIIa. Bond Distances (Å) and Angles (°) for α- and β-[Cu(*phen*)(*tpp*)BH_4] and [Cu(*phen*)(*tpp*)BD_4].

Bond	Distances		
	X-Ray (BH_4)		Neutron (BD_4) β-Red
	α-Yellow	β-Red	
Cu–B	2.28(1)	2.32(1)	2.29(2)
Cu–N(1)	2.12(1)	2.15(1)	2.15(2)
Cu–N(10)	2.149(7)	2.139(5)	2.11(2)
Cu–P	2.205(2)	2.227(2)	2.26(2)
N(1)–C(2)	1.32(1)	1.32(1)	1.31(2)
N(1)–C(14)	1.35(1)	1.36(1)	1.31(2)
C(2)–C(3)	1.42(2)	1.38(1)	1.42(2)
C(3)–C(4)	1.34(2)	1.33(1)	1.36(3)
C(4)–C(13)	1.39(1)	1.41(1)	1.43(3)
C(5)–C(6)	1.30(1)	1.29(1)	1.36(3)
C(5)–C(13)	1.44(2)	1.43(1)	1.42(3)
C(6)–C(12)	1.40(2)	1.47(1)	1.47(2)
C(7)–C(8)	1.33(2)	1.30(1)	1.36(2)
C(7)–C(12)	1.44(1)	1.39(1)	1.42(2)
C(8)–C(9)	1.42(2)	1.44(1)	1.43(2)
C(9)–N(10)	1.31(1)	1.32(1)	1.30(2)
C(11)–N(10)	1.34(1)	1.36(1)	1.37(2)

(continued overleaf)

TABLE IIIa. *(continued)*

Bond	Distances		
	X-Ray (BH_4)		Neutron (BD_4)
	α-Yellow	β-Red	β-Red
C(11)–C(12)	1.44(2)	1.41(1)	1.41(2)
C(11)–C(14)	1.44(1)	1.42(1)	1.41(2)
C(13)–C(14)	1.42(2)	1.42(1)	1.45(2)
P–C(21)	1.82(1)	1.82(1)	1.86(2)
P–C(31)	1.81(1)	1.83(1)	1.80(2)
P–C(41)	1.82(1)	1.83(1)	1.84(2)
C(21)–C(22)	1.39(1)	1.38(1)	1.39(2)
C(21)–C(26)	1.38(2)	1.40(1)	1.40(2)
C(22)–C(23)	1.43(2)	1.41(1)	1.39(2)
C(23)–C(24)	1.32(2)	1.37(1)	1.42(3)
C(24)–C(25)	1.33(1)	1.37(1)	1.38(2)
C(25)–C(26)	1.42(2)	1.38(1)	1.40(3)
C(31)–C(32)	1.37(1)	1.38(1)	1.40(2)
C(31)–C(36)	1.36(1)	1.39(1)	1.40(2)
C(32)–C(33)	1.45(1)	1.43(1)	1.42(2)
C(33)–C(34)	1.37(2)	1.38(1)	1.41(2)
C(34)–C(35)	1.35(2)	1.36(1)	1.41(2)
C(35)–C(36)	1.40(1)	1.41(1)	1.39(2)
C(41)–C(42)	1.39(1)	1.38(1)	1.42(2)
C(41)–C(46)	1.40(2)	1.38(1)	1.38(2)
C(42)–C(43)	1.40(2)	1.42(1)	1.45(3)
C(43)–C(44)	1.33(2)	1.34(1)	1.36(3)
C(44)–C(45)	1.41(2)	1.33(1)	1.43(3)
C(45)–C(46)	1.38(2)	1.41(1)	1.40(2)
Cu–D(1)			2.03(9)
Cu–D(2)			1.63(7)
B–D(1)			1.24(3)
B–D(2)			1.17(3)
B–D(3)			1.21(4)
B–D(4)			1.18(4)

Bond Angle	Angles		
	X-Ray (BH_4)		Neutron (BD_4)
	α-Yellow	α-Red	β-Red
B–Cu–N(1)	108.1(3)	110.2(3)	110.0(8)
B–Cu–N(10)	116.4(3)	125.2(3)	126.2(8)
B–Cu–P	120.3(3)	118.0(2)	116.7(9)
N(1)–Cu–N(10)	78.1(3)	77.6(2)	77.9(5)
N(1)–Cu–P	117.0(2)	109.7(1)	109.6(6)
N(10)–Cu–P	109.6(2)	108.4(1)	109.0(7)
Cu–N(1)–C(2)	128.5(7)	128.7(5)	127.8(11)
Cu–N(1)–C(14)	114.2(5)	112.6(4)	112.5(9)
C(2)–N(1)–C(14)	117.2(8)	118.1(6)	119.3(12)
N(1)–C(2)–C(3)	123.1(8)	124.0(8)	126(1)
C(2)–C(3)–C(4)	119.1(8)	118.4(9)	116(1)
C(3)–C(4)–C(13)	120.2(11)	122.0(8)	121(1)
C(6)–C(5)–C(13)	123.1(12)	122.0(8)	121(1)
C(5)–C(6)–C(12)	122.4(13)	122.5(8)	120(1)
C(8)–C(7)–C(12)	122.5(12)	121.0(8)	114(2)
C(7)–C(8)–C(9)	118.6(10)	119.5(8)	125(1)
C(8)–C(9)–N(10)	122.3(12)	133.4(7)	121(1)
C(9)–N(10)–Cu	127.7(8)	128.6(5)	128.6(9)

(continued on facing page)

TABLE IIIa. *(continued)*

Bond Angle	Angles		
	X-Ray (BH_4)		Neutron (BD_4)
	α-Yellow	α-Red	β-Red
C(11)–N(10)–Cu	112.2(4)	113.2(4)	112.3(8)
C(9)–N(10)–C(11)	119.9(9)	116.9(6)	118.2(11)
C(12)–C(11)–N(10)	122.9(7)	122.8(6)	122.7(12)
C(14)–C(11)–N(10)	118.7(8)	117.1(6)	117.6(12)
C(12)–C(11)–C(14)	118.3(9)	120.1(6)	119.6(12)
C(6)–C(12)–C(7)	127.7(11)	125.5(8)	121(2)
C(6)–C(12)–C(11)	118.6(8)	117.1(7)	119(2)
C(7)–C(12)–C(11)	113.6(11)	117.3(7)	120(2)
C(4)–C(13)–C(5)	125.5(11)	125.9(7)	124(2)
C(4)–C(13)–C(14)	117.2(10)	115.7(7)	117(2)
C(5)–C(13)–C(14)	117.3(7)	118.4(7)	119(2)
N(1)–C(14)–C(11)	116.6(8)	118.2(6)	118.6(11)
N(1)–C(14)–C(13)	116.6(8)	121.8(6)	121.0(12)
C(13)–C(14)–C(11)	120.1(8)	119.9(6)	120.3(13)
C(21)–P–Cu	114.7(3)	119.0(2)	119.1(8)
C(21)–P–C(31)	103.6(4)	103.6(3)	104.1(10)
C(21)–P–C(41)	102.9(4)	103.9(3)	104.7(10)
C(31)–P–Cu	115.7(3)	111.7(2)	112.1(9)
C(31)–P–C(41)	103.6(4)	104.4(3)	104.1(8)
C(41)–P–Cu	114.7(3)	112.8(2)	111.4(9)
P–C(21)–C(22)	116.3(8)	118.8(4)	117.8(13)
P–C(21)–C(26)	124.1(6)	122.8(4)	120.7(10)
C(22)–C(21)–C(26)	119.6(10)	118.4(5)	121(1)
C(23)–C(22)–C(21)	117.4(10)	120.9(5)	119(2)
C(22)–C(23)–C(24)	121.9(9)	119.1(5)	121(1)
C(23)–C(24)–C(25)	120.1(12)	120.1(6)	119(2)
C(24)–C(25)–C(26)	120.1(12)	120.1(6)	122(2)
C(25)–C(26)–C(21)	119.7(8)	120.5(5)	118.2(12)
P–C(31)–C(32)	115.8(6)	116.2(4)	115.6(10)
P–C(31)–C(36)	125.5(5)	124.7(5)	125.2(11)
C(32)–C(31)–C(36)	118.7(7)	119.1(6)	119.2(11)
C(33)–C(32)–C(31)	121.0(9)	121.4(6)	121.1(1)
C(32)–C(33)–C(34)	118.2(9)	117.2(8)	120(2)
C(33)–C(34)–C(35)	120.0(9)	121.7(7)	118(1)
C(34)–C(35)–C(36)	120.7(10)	120.5(6)	122(1)
C(35)–C(36)–C(31)	120.5(8)	119.8(6)	120(1)
P–C(41)–C(42)	124.8(8)	124.1(5)	122(1)
P–C(41)–C(46)	117.2(6)	116.7(5)	117(1)
C(42)–C(41)–C(46)	118.0(8)	118.9(6)	120(1)
C(43)–C(42)–C(41)	120.5(12)	119.2(7)	119(2)
C(42)–C(43)–C(44)	121.0(11)	120.1(8)	119(2)
C(43)–C(44)–C(45)	120.1(11)	122.2(8)	121(2)
C(44)–C(45)–C(46)	119.6(13)	119.1(7)	120(2)
C(45)–C(46)–C(41)	120.8(9)	120.6(6)	120(1)
D(1)–Cu–D(2)			62.3(10)
D(1)–Cu–N(1)			128.9(10)
D(1)–Cu–N(10)			100.7(9)
D(1)–Cu–P			118.6(10)
D(2)–Cu–N(1)			84.6(9)
D(2)–Cu–N(10)			137.9(10)
D(2)–Cu–P			112(6)
D(1)–B–Cu			48.3(11)
D(1)–B–D(2)			112(2)
D(1)–B–D(3)			110(3)

(continued overleaf)

TABLE IIIa. *(continued)*

Bond Angle	Angles		
	X-Ray (BH_4)		Neutron (BD_4)
	α-Yellow	α-Red	β-Red
D(1)–B–D(14)			103(3)
D(2)–B–Cu			65(2)
D(2)–B–D(3)			106(3)
D(2)–B–D(4)			116(3)
D(3)–B–D(4)			110(3)
Cu–D(1)–B			100(2)
Cu–D(2)–B			85(2)

TABLE IIIb. Comparative Bond Distances (Å) and Angles (°) for [Cu(*dmdp*)BH_4] and [Cu(*dmp*)BH_4] [4].

	Distances	
	[Cu(*dmdp*)BH_4]	[Cu(*dmp*)BH_4]
Cu–B	2.116(12)	2.080(15)
Cu–N(1)	2.026(10)	2.049(8)
Cu–N(10)	2.064(11)	2.023(9)
Cu–HB(1)	1.50(5)	1.58(5)
N(1)–C(2)	1.324(17)	1.324(11)
N(1)–C(11)	1.394(17)	1.369(13)
C(2)–C(3)	1.425(17)	1.392(14)
C(2)–C(21)	1.499(19)	1.465(15)
C(3)–C(4)	1.413(16)	1.349(16)
C(4)–C(12)	1.432(17)	1.385(15)
C(4)–C(41)	1.476(17)	
C(5)–C(6)	1.389(17)	1.334(15)
C(5)–C(12)	1.345(17)	1.426(15)
C(6)–C(13)	1.393(16)	1.432(14)
C(7)–C(8)	1.354(21)	1.369(14)
C(7)–C(13)	1.436(18)	1.396(15)
C(7)–C(71)	1.459(18)	
C(8)–C(9)	1.379(20)	1.409(15)
C(9)–N(10)	1.344(18)	1.300(11)
C(9)–C(91)	1.475(21)	1.465(13)
C(11)–C(12)	1.450(15)	1.384(13)
C(11)–C(14)	1.428(18)	1.429(14)
C(13)–C(14)	1.389(19)	1.395(13)
C(14)–N(10)	1.408(17)	1.363(11)
C(41)–C(42)	1.353(21)	
C(41)–C(46)	1.414(20)	
C(42)–C(43)	1.400(19)	
C(43)–C(44)	1.414(22)	
C(44)–C(45)	1.358(26)	
C(45)–C(46)	1.425(20)	
C(71)–C(72)	1.418(21)	
C(71)–C(76)	1.418(22)	
C(72)–C(73)	1.372(20)	
C(73)–C(74)	1.372(24)	
C(74)–C(75)	1.352(23)	
C(75)–C(76)	1.451(21)	
B–Cu–N(1)	140.8(5)	134.7(5)[a]

TABLE IIIb. *(continued)*

	Angles	
	[Cu(*dmdp*)BH_4]	[Cu(*dmp*)BH_4]
B–Cu–N(10)	136.3(4)	143.6(5)[a]
N(1)–Cu–N(10)	82.6(5)	81.8(3)
Cu–N(1)–C(2)	128.6(9)	130.5(8)
Cu–N(1)–C(11)	111.5(8)	112.3(7)
C(2)–N(1)–C(11)	119.9(10)	117.3(10)
N(1)–C(2)–C(3)	121.4(11)	121.7(12)
N(1)–C(2)–C(21)	118.1(11)	120.0(10)
C(3)–C(2)–C(21)	120.5(11)	118.4(11)
C(2)–C(3)–C(4)	120.4(10)	121.7(12)
C(3)–C(4)–C(12)	119.7(10)	120.0(13)
C(3)–C(4)–C(41)	118.7(11)	
C(12)–C(4)–C(41)	121.4(11)	
C(6)–C(5)–C(12)	121.2(11)	123.3(11)
C(5)–C(6)–C(13)	122.7(12)	117.9(12)
C(8)–C(7)–C(13)	118.8(11)	120.7(12)
C(8)–C(7)–C(71)	119.9(12)	
C(13)–C(7)–C(71)	121.2(12)	
C(7)–C(8)–C(9)	123.4(13)	118.8(11)
C(8)–C(9)–N(10)	119.8(12)	122.0(11)
C(8)–C(9)–C(91)	123.9(14)	119.1(12)
N(10)–C(9)–C(91)	115.9(13)	119.0(11)
C(9)–N(10)–Cu	130.0(9)	128.8(8)
C(14)–N(10)–Cu	111.5(8)	112.1(7)
C(9)–N(10)–C(14)	118.2(11)	119.1(10)
C(12)–C(11)–N(1)	122.9(10)	124.4(11)
C(12)–C(11)–C(14)	118.4(11)	120.0(11)
C(14)–C(11)–N(1)	118.6(10)	115.7(10)
C(4)–C(12)–C(5)	125.5(11)	125.4(11)[a]
C(4)–C(12)–C(11)	115.6(10)	120.0(11)
C(5)–C(12)–C(11)	118.9(11)	118.8(11)
C(6)–C(13)–C(7)	126.7(12)	122.5(11)[a]
C(6)–C(13)–C(14)	117.3(12)	121.4(12)
C(7)–C(13)–C(14)	115.9(11)	116.1(12)
N(10)–C(14)–C(11)	115.4(12)	118.1(10)
N(10)–C(14)–C(13)	123.4(2)	123.2(11)
C(11)–C(14)–C(13)	121.2(12)	118.7(11)
C(4)–C(41)–C(42)	124.6(12)	

TABLE IIIb. *(continued)*

	Angles	
	[Cu(*dmdp*)BH_4]	[Cu(*dmp*)BH_4]
C(4)–C(41)–C(46)	116.6(13)	
C(42)–C(41)–C(46)	118.2(12)	
C(41)–C(42)–C(43)	122.3(13)	
C(42)–C(43)–C(44)	119.0(15)	
C(43)–C(44)–C(45)	120.3(15)	
C(44)–C(45)–C(46)	119.7(14)	
C(41)–C(46)–C(45)	120.2(14)	
C(7)–C(71)–C(72)	123.7(14)	
C(7)–C(71)–C(76)	118.5(13)	
C(72)–C(71)–C(76)	117.8(13)	
C(71)–C(72)–C(73)	120.8(15)	
C(72)–C(73)–C(74)	121.8(16)	
C(73)–C(74)–C(75)	120.1(14)	
C(74)–C(75)–C(76)	120.7(15)	
C(71)–C(76)–C(75)	118.6(14)	

[a] Listed value in error [4].

confirmed from statistics, (mean $|E^2 - 1| = 0.66$). Most of the hydrogen atoms were found from a difference-Fourier synthesis, and included in the refinement at fixed positions with their isotropic U's set invariant at 0.05 Å^2.

The scattering factors used in all the X-ray structures were those in [6] for the non-hydrogen atoms and those in [7] for the hydrogens. The neutron scattering lengths used were those in Table 1, [8]. Atomic parameters and interatomic distances and angles are in Tables II and III respectively. Lists of H atomic coordinates, structure factors and anisotropic thermal parameters have been submitted. Copies may be obtained from the authors.

Discussion

With Cu^I, BH_4^- bonds in a variety of ways, *i.e.* as a monodentate ligand in Cu(*mdpp*)$_3BH_4$, (*VII*), (*mdpp* = methyldiphenylphosphine): Cu–H, 1.47; Cu–B, 2.518(3) Å, neutron, [9]; in (*VII*), Cu–H, 1.697(5); Cu–B, 2.650(5) Å, X-ray, [10]; and in Cu(*triphos*)BH_4, (*triphos* = 1,1,1-tris((diphenylphosphino)methyl)ethane), Cu–H, 1.60(4); Cu–B, 2.44(2) Å [11]; as a bidentate ligand in (*V*), Cu–H, 1.58(5), Cu–B, 2.08(1) Å [4]; and in (*VI*), Cu–H, 2.02(5); Cu–B, 2.184(9) Å [12]. In the current study of Cu^I borohydrides, BH_4^- behaves as a bidentate ligand.

The redetermination of the α-form, (*II*), has only marginally improved the precision of the atomic parameters compared to those reported in [2]. A problem has been to locate the BH_4^- hydrogen atoms using conventional difference-Fourier syntheses. Bau *et al.* [13] have been successful in locating hydrogen in metal hydrides using exclusively low angle data. However, the technique available in SHELX did not completely resolve the problem, although it has been quite successful on other occasions.

The neutron refinement for the β-form unequivocally located the BD_4^- group linked to the metal atom. Assuming that these deuterium atoms occupy similar locations to the hydrogen atoms in (*III*), then the results are significantly different from those previously reported for α [2].

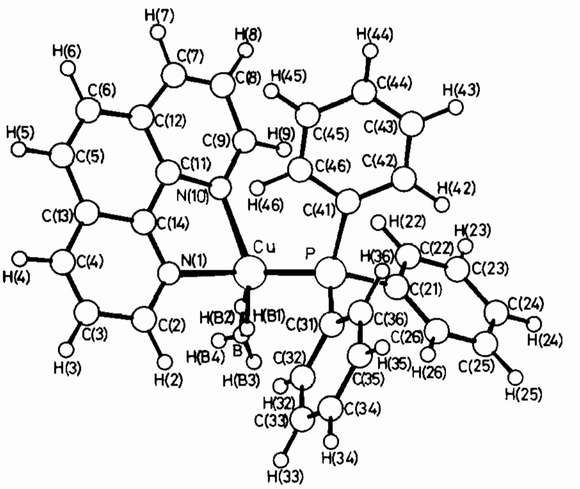

Fig. 1(a). Molecular conformation and atom nomenclature for α-[Cu(*phen*)(*tpp*)BH_4].

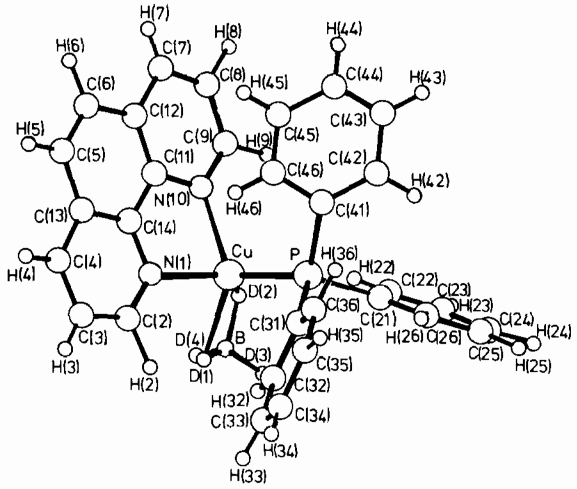

Fig. 1(b). Molecular conformation and atom nomenclature for β-[Cu(*phen*)(*tpp*)BD_4].

TABLE IV. Structural Differences between the α- and β-Forms.

	I α-form	II β-form	III β-form
Bond Distances (Å)	(X-ray)	(X-ray)	(neutron)
Cu–P	2.205(2)	2.227(2)	2.26(2)
Bond Angle (°)			
N(1)–Cu–P	117.0(2)	109.7(1)	109.6(6)*
N(10)–Cu–P	109.6(2)	108.4(1)	109.0(7)
Torsion Angles (°)			
Cu–P–C(21)–C(22)	+48.7	–21.3	–21.8*
Cu–P–C(21)–C(26)	–129.9	+159.2	+160.9*
Cu–P–C(31)–C(32)	+32.2	–41.7	–42.8
Cu–P–C(31)–C(36)	–146.5	+137.6	+136.7
Cu–P–C(41)–C(42)	–142.1	+129.4	+127.7
Cu–P–C(41)–C(46)	+38.0	–44.9	–44.5
B–Cu–N(1)–C(2)	+60.8	–56.8	–54.7
B–Cu–N(1)–C(14)	–115.3	+131.9	+132.8*

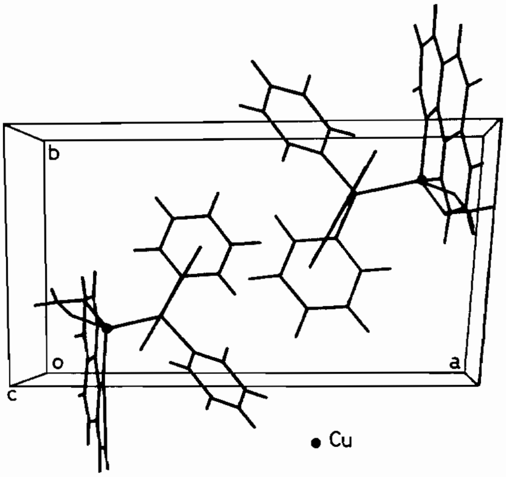

Fig. 2(a). Packing diagram perpendicular to the *ab* plane for α-[Cu(*phen*)(*tpp*)BH_4].

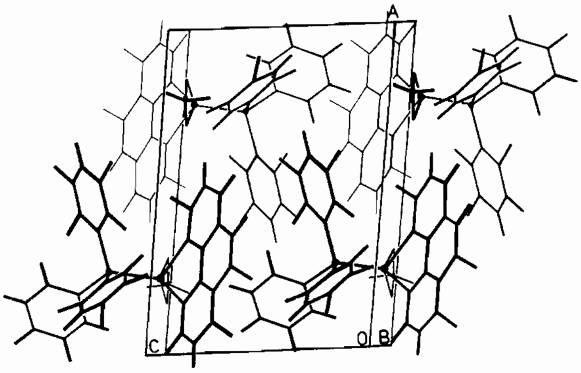

Fig. 2(b). Packing diagram perpendicular to the *ab* plane for β-[Cu(*phen*)(*tpp*)BD_4].

In both isomers, the BH_4^- moiety behaves as a bidentate ligand bonding through three-centered hydrogen bonds to distorted tetrahedral Cu(I) [B–Cu–N(1), 108.1(3), 110.0(8)°; B–Cu–N(10), 116(4), 126.2(8)°; B–Cu–P, 120.3(3), 116.7(9)°; N(1)–Cu–N(10), 78.1(3), 77.9(5)°; N(1)–Cu–P, 117.0(2), 109.6(6)°; N(10)–Cu–P, 109.6(2), 109.0(7)°], in (*II*) and (*III*), respectively, and [Cu–D_b, 2.03(9), 1.63(7) Å; B–D_b, 1.24(3), 1.17(3) Å; Cu–B 2.29(2) Å], in (*III*). The remaining two deuterium atoms are in terminal positions [B–D_t, 1.21(4), 1.18(4) Å], (*III*). Further comparisons between (*II*) and (*III*) are listed in Table IV. Triphenylphosphine completes the Cu(I) coordination sphere [Cu–P, 2.205(5), 2.26(2) Å], in (*II*)and (*III*), respectively.

The Cu(I)–B distance is short in the (2,9-dimethyl-4,7-diphenyl) substituted phenanthroline complex, (*IV*) [Cu–B, 2.116(12) Å; Cu–N, 2.026(10), 2.064(11) Å]. The Cu(I) coordination remains tetrahedral because the 2,9-dimethyl groups prevent further bonding by additional ligands. In the unsubstituted examples, (*II*) and (*III*), additional bonding is possible by *tpp* due to redistribution of the copper *dπ* back donation from the conjugated *phen* and borohydride to the phosphine ligand. This weakens the bonds, [Cu–B, 2.29(2); Cu–N, 2.11(2), 2.15(2) Å]. The reduced stability of these five coordinate Cu(I) species in solution, and the change in the charge transfer maxima between the Cu and the *phen* to lower energy (orange to red) confirms this. These effects are caused by the distribution of bulk about the copper [14]. With a further increase in ligand bulk, in compound (*VII*), [9], the Cu–B bond [Cu–B, 2.498(5) to 2.650(5) Å] is further weakened and is singly bound. However, there is one long B–H_t bond directed to the copper, [Cu–H, 2.922(7) Å]. Even though this hydrogen is not bound to the copper, it is still attempting to achieve the unsymmetrical bidentate bonding evident in (*II*)and (*III*).

In the examples (*II*), (*III*) and (*VI*), the copper–phosphine bond [Cu–P, 2.26(2) Å] remains unchanged. This is comparable to those found in *μ*-tetrahydroboratobis[bis(triphenylphosphine)copper-(*I*)] perchlorate, (*VIII*), [Cu–P, 2.256(2), 2.260(2) Å], [15], [2.276(1) Å], in (*VI*), [12], and [2.180(2) Å], in (*I*), [1]. The 8° widening of the N(1)–Cu–P [117.0(2)°-, (*II*) compared to [109.6(1)°], (*III*),

TABLE V. The Infrared Spectra of the $CuBH_4$ in [Cu(*phen*)(*tpp*)BH_4] and [Cu(*dmdp*)BH_4].

[Cu(*phen*)(*tpp*)BH_4]		Assignment	[Cu(*dmdp*)BH_4]
Solid	Solution		Solid
2360s	2380s	B–H_t stretch	2385s
2330s	2342s	B–H_t stretch	2350s
2245w	2245w	H–B–H terminal overtone	2245w
2070s	1965s	B–H_b stretch	1982s
1910w	1900sh	B–H_b stretch	1905sh
1120s	1182s	H–B–H terminal deformation	1128s
	995w	H–B–H bend	960w
	513m	$CuBH_4$	398m

is mirrored by a similar 9° closing in B–Cu–N(10) [116.4(3)°], (*II*); 126.2(8)°], (*III*). This indicates that BH_4^- readily compensates for changes in its neighbouring ligands.

It should be noted that the α and β forms crystallize from nonpolar and polar solvents respectively, and their structural differences are indicated by (*) in Table IV. These differences are further shown in the packing diagrams for the α- and β-forms in Figs. 2(a) and (b).

The metal atom is five coordinate for both isomers. The variety of steric factors confirms that the unusual bands in the νB–H_t and νB–H_b regions of the infrared (Table V) are due to the unsymmetrical bidentate bonding [Cu–D, 1.63(7), 2.03(8) Å and D–Cu–D, 62.3(10)°]. Another example of an unsymmetrical bidentate BH_4^- has been found in $(MeC_5H_4)_2Hf(BH_4)_2$, [Hf–H, 2.069(7), 2.120(8) Å; H–Hf–H, 57.0(3)°], [16]. The unsymmetrical nature of the H-bridge bonds (νB–H_b 2100 cm^{-1}) causes a degeneration of the bridge mode accompanied by an expected reduction in intensity. The locations of the BH_4^- vibrations were confirmed by the shift ratio (ν_H/ν_D = 1.3) on deuteration. Little variation was seen between the two forms in the solid spectra. In confirmed doubly bridged species (*V*), [17], this νB–H_b band is generally comparable in intensity to νB–H_t. Also, there was no band at 1060 cm^{-1}, which is indicative of a singly bridged species [18]. The infrared spectrum indicates that the BH_4^- is tightly constrained in the solid form by the triphenylphosphine and the phenanthroline, preventing νB–H_b attaining its usual vibrational strength. On addition of a polar solvent such as methylene chloride, chloroform, dimethylsulphoxide or pyridine, νB–H_b becomes more intense, coinciding with an observed colour change to that of the β-form.

The solid crystal structure indicates a slight difference in the Cu–P bond [2.205(2) Å, (*II*); 2.26(2) Å, (*III*)]. A reorientation of the phenyl rings probably allows the BH_4^- group to attain its expected vibration for a symmetrical double bridged species in solution even though this is not evident in the solid state infrared.

Another possible explanation is that the labile *tpp* ligand dissociates in solution. This is more likely. The phosphorus signal in the ^{31}P NMR does not split into an expected doublet on the addition of free *tpp*, but the whole peak shifts towards that of free *tpp*. The magnitude of the shift depends on the amount of free *tpp* added.

Compound (*IV*) is tetrahedral with a similar stereochemistry to that found for (*V*), [4]. [N–Cu–N, 83.6(5)°; 81.8(3)°; H–Cu–H′, 102(3); 77(2)°; N–Cu–H, 147(1), 148(1)°; 124.0(10), 128.5(10)°] for (*IV*) and (*V*), respectively. The bonding involves two N atoms from the substituted *phen* ligands [Cu–N, 2.025(19), 2.064(11) Å; 2.023(9), 2.049(8) Å] and two symmetrically bound H atoms from a BH_4^- ligand [Cu–H, 1.50(5); 1.58(5) Å]. The labelling of the atoms is illustrated in Fig. 3. The difference between this compound and (*V*) is the substitution of phenyl groups at the 4- and 7- positions. The bond distances and angles are similar. The electron withdrawing nature of the phenyl groups is dissipated in the delocalised phenanthroline system. The presence of the phenyl groups at the 4- and 7- positions appears to have induced *cis*-stacking, Fig. 4, of the planar molecules perpendicular to the *c*-axis, with 3.85 Å separation. This distance is greater than the corresponding one found for (*V*), (3.40 Å) where the stacking is *trans*. Analysis of the atomic parameters indicates a pseudo two-fold axis through the molecule. The phenyl torsion angles are [C(3)–C(4)–C(41)–C(42), –130.2°; C(3)–C(4)–C(41)–C(46), +44.9°; C(8)–C(7)–C(71)–C(72), +136.4°; C(8)–C(7)–C(71)–C(76), –41.8°]. The molecule could not be relocated

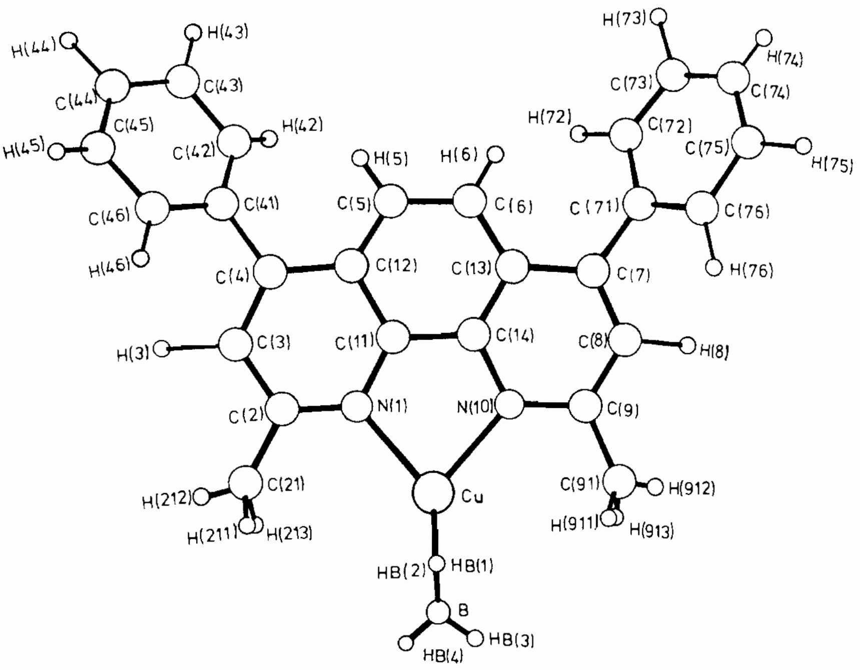

Fig. 3. Molecular conformation and atom nomenclature for [Cu(*dmdp*)BH_4].

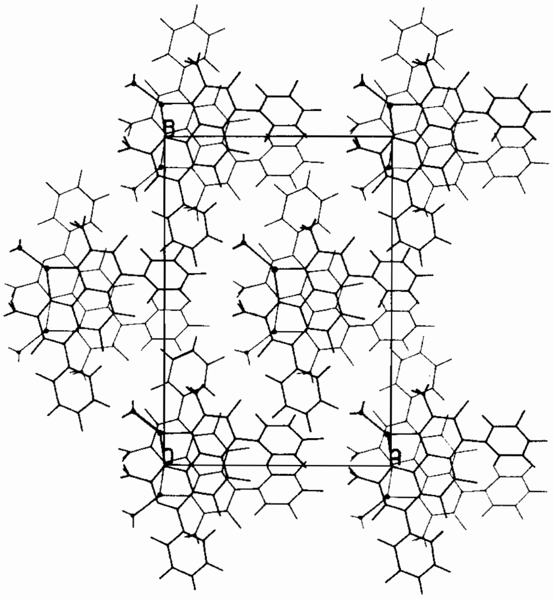

Fig. 4. Packing diagram perpendicular to the *ab* plane for [Cu(*dmdp*)BH_4].

about a crystallographic two-fold axis in the space group *C*2/*c*, $Z = 4$. This justified the choice of the non-centrosymmetric space group *Cc*.

The B (0.52 Å) and Cu (0.16 Å) lie above the N(1)–C(11)–C(14)–N(10) plane in (*IV*), compared to being in this plane in (*V*). This is probably a function of BH_4^- packing. In its *trans* orientation in (*V*), the boron experiences stronger interaction with the neighbouring molecules because of the reduced distance. This interaction forces the boron and the copper to stay in the plane. The two methyl groups in the 2,9-positions protect the BH_4^- within the molecule and allow symmetrical bridging bonding. Both compounds (*IV*) and (*V*) exhibit unusual thermal stability in CH_3CN and benzonitrile compared to other solvents such as chloroform, acetone and ethanol. This probably indicates the copper has a fifth bonding site available, although compounds of this type have not yet been isolated. However, a similar bond has been found for Cu(I) in the bidentate acrylonitrile π-complex of cuprous chloride, [Cu–N 2.08 Å; Cu–C 2.06, 2.13 Å], [19]. Both compounds (*IV*) and (*V*) are good examples of a symmetrical bidentate BH_4^- Cu(I) system.

Acknowledgements

The authors wish to thank the University of Queensland and the Australian Institute for Nuclear Science and Engineering (AINSE) for financial support; the University of Western Australia and AINSE for data collection facilities, and the Queensland Institute of Technology for leave for one of us (G.S.) to work on this project.

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