The previous ambiguity in the space-group assignment has been resolved, the centrosymmetric assignment $P6_3/m$ being quite definite. Thus the space-group assignment for barium perbromate trihydrate [which was tested in the same manner as described above for the perchlorate and with the same results (private communication, R. E. Gerkin)] is indeed the same as that for barium perchlorate trihydrate, as surmised previously by Gerkin, Reppart & Appelman (1988).

Although in general terms the structure presented by Mani & Ramaseshan (1960) is in good accord with the present determination, there are numerous differences in detail. Since the previous description was based on photographic observations of 152 unique reflections and the final R value achieved was 0·22, the present description entirely supersedes it with respect to quantitative details.

On the basis of the present results it appears most likely that the water molecule H atoms in the $Ba(BrO_4)_2.3H_2O$ structure also lie entirely in the planes at $z = \frac{1}{4}$ and $\frac{3}{4}$ rather than out of the plane as surmised by Gerkin, Reppart & Appelman (1988). Indeed, re-examination of the final electron density difference map for that structure revealed a peak at $x = 0·32$, $y = 0·31$, $z = \frac{1}{4}$ of appropriate magnitude for an H atom and approximately 1 Å from O(3). This is particularly suggestive since H(2) as assigned here in the perchlorate should appear in the perbromate at $x = 0·305$, $y = 0·320$, $z = \frac{1}{4}$. Since no second corresponding peak was observed in the difference list, however, no

least-squares refinement of H-atom positions in the perbromate has been pursued.

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Structure of Bis[hydrotris(3,5-dimethyl-1-pyrazolyl)borato]copper(II)

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Abstract. $[Cu(C_{15}H_{22}BN_6)_2]$, $M_r = 658·03$, triclinic, $P\bar{1}$, $a = 10·201$ (1), $b = 10·875$ (1), $c = 8·787$ (1) Å, $\alpha = 83·68$ (1), $\beta = 101·62$ (1), $\gamma = 117·59$ (1)°, $V = 846·1$ (2) Å^3, $D_x = 1·30$ g cm^{-3}, $Z = 1$, $T = 298$ K, $F(000) = 347$, $\mu(Cu K\alpha) = 11·04$ cm^{-1}, $\lambda = 1·5418$ Å, $R = 0·052$ for 2285 observed reflections. The copper

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atom is coordinated octahedrally by six nitrogen atoms from the ligands, HB(3,5-Me$_2$pz)$_3$. The CuN$_6$ chromophore is an elongated rhombic octahedron.

Introduction. The synthesis of copper complexes having nitrogen ligands has received much attention as these complexes are synthetic analogs of the coordination sites of copper proteins such as hemocyanin (Gaykema, Hol, Vereijken, Soeter, Bak & Beintema, 1984). Among many ligands designed for this purpose, hydrotris(3,5-dimethyl-1-pyrazolyl)borate, HB(3,5-Me$_2$pz)$_3$, is one of the most attractive since it has a strong capability of ligating copper through the three pyrazolyl nitrogen atoms and of stabilizing the isolable complexes owing to its bulkiness (Thompson, Marks & Ibers, 1977; Thompson, Harlow & Whitney, 1983; Thompson, 1984). During the course of our efforts to synthesize novel copper complexes with HB(3,5-Me$_2$pz)$_3$, it was noted that bis[hydrotris(3,5-dimethyl-1-pyrazolyl)-borato]copper(II), (1), was readily formed. The crystal structure of the corresponding complex with hydrotris(1-pyrazolyl)borate, HBpz$_3$, has already been reported (Murphy, Hathaway & King, 1979). Herein, the crystal structure of (1) is described.

Experimental. Cu(CO)HB(3,5-Me$_2$pz)$_3$ prepared by the literature method (Mealli, Arcus, Wilkinson, Marks & Ibers, 1976) was reacted with 1·5 equivalent amount of iodosobenzene in CH$_2$Cl$_2$ to give [CuHB(3,5-Me$_2$pz)$_3$]$_2$O, (2) (Kitajima, Koda & Moro-oka, 1988). (2) was dissolved in methanol and left exposed to the air for two weeks to give blue-green crystals of (1). Approximate dimensions of crystal 0·2 × 0·2 × 0·2 mm, Rigaku AFC-4 diffractometer, Cu $K\alpha$ radiation, graphite monochromator; cell parameters refined by least-squares method on the basis of 15 independent 2θ values ($42 < 2\theta < 56°$); intensity measurements performed up to $2\theta = 125°$, ω–2θ scan, scan speed 4° (θ) min^{-1}; scan width $(1·0 + 0·15\tan\theta)°$, 2341 reflections measured, 2285 intensities with $|F_o| > 3(|F_o|)$ considered as observed; correction for Lorentz and polarization, absorption ignored; direct method (*MULTAN*78, Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978); full-matrix least squares with *SHELX*76 program (Sheldrick, 1976), $\sum w(|F_o| - |F_c|)^2$ minimized, $w = [\sigma^2(|F_o|) + (c|F_o|)^2]^{-1}$, $c = 0·065$; H atoms on the pyrazole rings appeared in the difference map, H atoms on the methyl groups were fixed by geometrical constraints (C–H = 1·0 Å), final $R = 0·052$, $wR = 0·062$ for 2285 observed reflections; $\Delta\rho_{max} < 0·5$ e Å^{-3}; $(\Delta/\sigma)_{max} = 0·53$; atomic scattering factors from *International Tables for X-ray Crystallography* (1974); calculations carried out on the FACOM-HITAC system M-280H computer at this Institute.

Table 1. *Final atomic coordinates* (× 10^4) *with their estimated standard deviations and equivalent isotropic thermal parameters*

$$B_{eq} = \tfrac{4}{3}\sum_i\sum_j B_{ij}a_i^*a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	B_{eq}(Å^2)
Cu	8716	10035	693	4·1
N(1)	9521(5)	12002(5)	1730(7)	4·4
N(2)	9845(5)	13122(4)	701(7)	3·9
N(3)	7428(4)	10607(4)	-981(6)	3·3
N(4)	8060(5)	11870(5)	-1618(6)	3·6
N(5)	10489(6)	11054(5)	-826(8)	5·2
N(6)	10771(5)	12394(4)	-1234(6)	3·9
N(7)	7942(5)	8050(5)	-270(7)	3·5
N(8)	7570(5)	6897(5)	705(6)	3·6
N(9)	10043(5)	9480(4)	2393(6)	3·7
N(10)	9348(5)	8156(4)	3125(6)	3·2
N(11)	6872(5)	8947(5)	2241(7)	4·1
N(12)	6583(5)	7615(5)	2717(7)	4·4
C(1)	9511(10)	11503(9)	4560(10)	5·6
C(2)	9789(9)	12467(11)	3181(13)	7·2
C(3)	10366(7)	13925(7)	3085(10)	4·7
C(4)	10344(7)	14348(6)	1540(11)	4·9
C(5)	10768(9)	15784(7)	933(12)	6·1
C(6)	4888(7)	8537(6)	-1418(11)	5·5
C(7)	6036(6)	9983(6)	-1689(8)	4·3
C(8)	5826(8)	10895(8)	-2935(10)	5·3
C(9)	7039(6)	12042(5)	-2799(7)	3·5
C(10)	7423(10)	13333(7)	-3728(10)	5·8
C(11)	11645(13)	9420(10)	-707(16)	8·8
C(12)	11609(7)	10808(9)	-1049(10)	5·9
C(13)	12671(7)	12226(11)	-1800(11)	6·7
C(14)	12190(6)	13007(8)	-1734(9)	5·3
C(15)	12764(9)	14538(9)	-2263(18)	9·6
C(16)	7839(11)	8515(10)	-3162(11)	6·8
C(17)	7669(6)	7610(6)	-1691(8)	3·7
C(18)	7158(11)	6184(11)	-1604(15)	7·0
C(19)	7083(7)	5803(6)	-115(11)	4·5
C(20)	6537(11)	4377(7)	697(11)	6·1
C(21)	12481(7)	11592(7)	2718(11)	5·7
C(22)	11446(6)	10099(6)	3186(8)	4·3
C(23)	11731(6)	9258(6)	4249(9)	4·5
C(24)	10318(7)	8030(7)	4233(10)	4·8
C(25)	10015(9)	6769(8)	5351(11)	5·9
C(26)	5712(9)	10456(9)	2395(14)	6·7
C(27)	5747(9)	9060(8)	2668(11)	5·7
C(28)	4755(9)	7954(11)	3188(12)	6·5
C(29)	5402(7)	6943(8)	3335(10)	5·1
C(30)	4722(11)	5479(12)	3812(14)	8·7
B(1)	9738(7)	12952(7)	-1011(9)	3·5
B(2)	7752(6)	7117(5)	2408(11)	3·9

Discussion. The final atomic parameters for non-H atoms are in Table 1.* An *ORTEP* (Johnson, 1965) view of (1) is shown in Fig. 1. The copper atom is coordinated by the nitrogen atoms of six separate pyrazolyl rings. The CuN$_6$ chromophore is described as an elongated rhombic octahedron with considerable differences in the bond lengths (Table 2). Each HB(3,5-Me$_2$pz)$_3$ ligand is involved in three-coordination as a tripod ligand, but each ligand has serious distortion from the threefold symmetry of the free ligand, as shown in Table 2. Each ligand can be distinguished in terms of the electronic state of its pyrazolyl rings. The formal electronic state of the

pyrazolyl ring can be described in the following two forms.

(I)   (II)
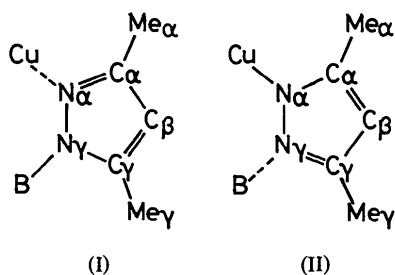
Table 2. *Bond lengths (Å) and bond angles (°)*

|			
Cu—N(1)	2·140 (6)	Cu—N(3)	2·013 (5)
Cu—N(5)	2·252 (7)	Cu—N(7)	2·133 (6)
Cu—N(9)	2·042 (6)	Cu—N(11)	2·324 (6)
B(1)—N(2)	1·512 (10)	B(1)—N(4)	1·583 (10)
B(1)—N(6)	1·489 (10)	B(2)—N(8)	1·502 (11)
B(2)—N(10)	1·538 (11)	B(2)—N(12)	1·597 (11)
C(1)—C(2)	1·494 (16)	C(4)—C(5)	1·481 (15)
C(6)—C(7)	1·492 (12)	C(9)—C(10)	1·469 (12)
C(11)—C(12)	1·522 (17)	C(14)—C(15)	1·538 (19)
C(16)—C(17)	1·523 (13)	C(19)—C(20)	1·530 (15)
C(21)—C(22)	1·536 (12)	C(24)—C(25)	1·541 (13)
C(26)—C(27)	1·527 (15)	C(29)—C(30)	1·462 (16)
N(1)—Cu—N(3)	87·6 (2)	N(1)—Cu—N(5)	88·6 (3)
N(3)—Cu—N(5)	85·7 (2)	N(7)—Cu—N(9)	86·4 (2)
N(7)—Cu—N(11)	87·1 (2)	N(9)—Cu—N(11)	86·1 (2)
Cu—N(1)—N(2)	115·2 (5)	Cu—N(3)—N(4)	118·1 (4)
Cu—N(5)—N(6)	112·8 (5)	Cu—N(7)—N(8)	119·0 (4)
Cu—N(9)—N(10)	117·3 (4)	Cu—N(11)—N(12)	115·7 (4)
Cu—N(1)—C(2)	136·4 (7)	Cu—N(3)—C(7)	134·2 (5)
Cu—N(5)—C(12)	133·0 (6)	Cu—N(7)—C(17)	134·0 (5)
Cu—N(9)—C(22)	136·8 (5)	Cu—N(11)—C(27)	141·4 (6)
N(2)—N(1)—C(2)	108·5 (7)	N(4)—N(3)—C(7)	107·6 (6)
N(6)—N(5)—C(12)	110·9 (7)	N(8)—N(7)—C(17)	107·0 (6)
N(10)—N(9)—C(22)	105·5 (5)	N(12)—N(11)—C(27)	101·7 (6)
N(1)—N(2)—C(4)	109·1 (6)	N(3)—N(4)—C(9)	109·8 (5)
N(5)—N(6)—C(14)	105·2 (6)	N(7)—N(8)—C(19)	109·0 (6)
N(9)—N(10)—C(24)	108·6 (6)	N(11)—N(12)—C(29)	115·1 (6)
N(1)—N(2)—B(1)	121·3 (6)	N(3)—N(4)—B(1)	121·9 (5)
N(5)—N(6)—B(1)	121·4 (6)	N(7)—N(8)—B(2)	117·6 (6)
N(9)—N(10)—B(2)	118·9 (5)	N(11)—N(12)—B(2)	115·7 (6)
C(4)—N(2)—B(1)	129·5 (7)	C(9)—N(4)—B(1)	128·3 (5)
C(14)—N(6)—B(1)	133·2 (6)	C(19)—N(8)—B(2)	133·4 (7)
C(24)—N(10)—B(2)	132·0 (6)	C(29)—N(12)—B(2)	129·2 (7)
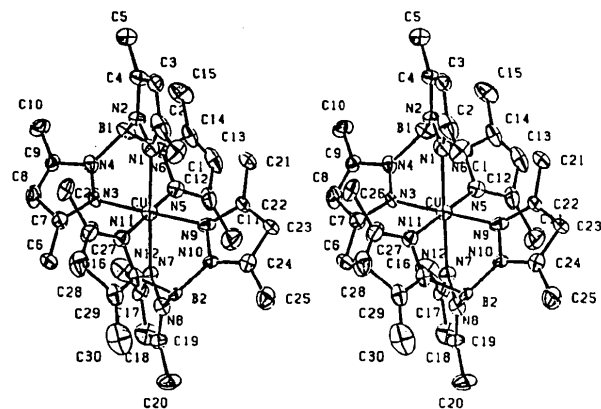
Fig. 1. Stereoview of (1). The atoms are represented by their 70% probability ellipsoids, and the hydrogen atoms have been omitted.

Table 3. *Average bond lengths (Å) in the pyrazole rings.*
$[L_1,$ *bonded to* $B(1);$ $L_2,$ *bonded to* $B(2)]$

	L_1	L_2
Cα—Nα	1·33 (1)	1·33 (1)
Cγ—Nγ	1·41 (1)	1·29 (1)
Cα—Cβ	1·48 (1)	1·33 (1)
Cβ—Cγ	1·28 (1)	1·43 (1)
Nα—Nγ	1·36 (1)	1·39 (1)

In the copper complexes with the $HB(3,5-Me_2pz)_3$ ligand so far reported (Thompson, Marks & Ibers, 1977; Thompson, Harlow & Whitney, 1983; Thompson, 1984; Mealli, Arcus, Wilkinson, Marks & Ibers, 1976), the bond distances Cα—Nα and Cγ—Nγ, or Cα—Cβ and Cβ—Cγ are reasonably close; implying that both canonical forms of the electronic state contribute to the structure. However, in (1) the average bond distances of the three pyrazolyl rings in each $HB(3,5-Me_2pz)_3$ show significant deviations, as summarized in Table 3. The electronic state of the rings in L_1 may be attributable to the form (I) whereas the bond distances in the other ligand (L_2) are almost consistent with the expected values for the form (II). The structural deviations of the present complex (1), which are not observed in the corresponding copper(II) complex with $HBpz_3$ (Murphy, Hathaway & King, 1979), are ascribed to the bulkiness of $HB(3,5-Me_2pz)_3$.

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