SHORT COMMUNICATIONS

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

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Abstract

The crystal structure of $Cu[HB(3,5-Me_2pz)_3]_2$, which was originally described in space group $P1$ [Kitajima, Moro-oka, Uchida, Sasada & Ohashi (1988). *Acta Cryst.* C**44**, 1876–1878], is properly described in $P\bar{1}$. Refinement in $P\bar{1}$ has led to a more reasonable structure in which all six pyrazole rings show effectively identical bond lengths. The coordination about Cu is distorted octahedral, with three unequal pairs of Cu—N distances of 2·020 (2), 2·142 (3) and 2·284 (3) Å.

Crystals of this compound, $Cu[HB(3,5-Me_2pz)_3]_2$, have recently been described as triclinic, space group $P1$, with $a = 10·201$ (1), $b = 10·875$ (1), $c = 8·787$ (1) Å, $\alpha = 83·68$ (1), $\beta = 101·62$ (1), $\gamma = 117·59$ (1)°, $Z = 1$ (Kitajima, Moro-oka, Uchida, Sasada & Ohashi, 1988; hereinafter, KMUSO). One peculiarity of the reported structure was large variations in the C—C and C—N bond lengths within the pyrazole rings, which prompted the authors to suggest that all three rings in one $HB(3,5-Me_2pz)_3$ ligand may exist in a single canonical form while the three rings in the second ligand may exist in the other principal canonical form. However, there were large ranges of values for equivalent C—C distances within a single ligand; for example, the three values of the $C_\alpha-C_\beta$ bond length were 1·41, 1·45 and 1·58 Å in ligand L_1 and 1·27, 1·32 and 1·39 Å in ligand L_2 [as calculated from the reported coordinates; all that is reported in KMUSO are the averaged values and inappropriate e.s.d.'s, 1·48 (1) and 1·33 (1) Å]. These surprising results were artifacts, resulting from the refinement of a centro-symmetric structure in a noncentrosymmetric space group.

The structure is appropriately described in space group $P\bar{1}$. After placing the origin at the Cu atom and averaging the coordinates of corresponding atoms in the two ligands, refinement in $P\bar{1}$ converged routinely to an R of 0·0469 for the 2285 F values recovered from SUP 51188, compared with the R of 0·052 reported by KMUSO (also for 2285 reflections); the number of parameters was 206 in $P\bar{1}$ and, presumably, 435 in $P1$. Included in the $P\bar{1}$ model was a secondary-extinction coefficient [Larson (1967); equation (3)] of 13·5 (4) × 10⁻⁶, which may have accounted for some of the improvement in R. Calculations were carried out on a

VAX 11/750 computer under the *CRYM* system of programs. The quantity minimized was $\sum w(F_o^2 - F_c^2)^2$; since values of $\sigma(F_o)$ were not included in SUP 51188, weights were assigned according to Hughes (1941); see also Marsh & Schomaker (1979).

Table 1. *Coordinates, space group $P\bar{1}$; x, y, z and $U_{eq} \times 10^4$*

$$U_{eq} = \tfrac{1}{3}\sum_i\sum_j[U_{ij}(a_i^* a_j^*)(\mathbf{a}_i.\mathbf{a}_j)].$$

	x	y	z	U_{eq} (Å²)
Cu	0	0	0	466 (2)
N(1)	786 (3)	1978 (3)	1007 (3)	552 (8)
N(2)	1141 (3)	3114 (2)	0 (3)	520 (7)
N(3)	−1299 (3)	560 (2)	−1688 (3)	492 (6)
N(4)	−633 (3)	1861 (2)	−2364 (3)	479 (6)
N(5)	1809 (3)	1050 (3)	−1526 (3)	647 (7)
N(6)	2095 (3)	2390 (3)	−1966 (3)	569 (7)
C(1)	823 (5)	1507 (5)	3838 (5)	869 (14)
C(2)	1064 (4)	2436 (4)	2437 (5)	648 (11)
C(3)	1601 (4)	3867 (4)	2354 (5)	748 (12)
C(4)	1638 (4)	4273 (3)	835 (5)	646 (10)
C(5)	2113 (5)	5690 (4)	73 (5)	932 (13)
C(6)	−3805 (4)	−1531 (3)	−2070 (5)	795 (11)
C(7)	−2712 (3)	−70 (3)	−2440 (4)	575 (8)
C(8)	−2958 (4)	814 (4)	−3594 (4)	676 (10)
C(9)	−1645 (4)	2010 (3)	−3527 (4)	581 (8)
C(10)	−1281 (5)	3289 (4)	−4534 (5)	841 (12)
C(11)	2986 (5)	−486 (5)	−1540 (6)	1166 (15)
C(12)	2950 (4)	891 (4)	−1863 (5)	803 (11)
C(13)	3942 (4)	2106 (5)	−2482 (5)	925 (14)
C(14)	3397 (4)	3042 (4)	−2522 (5)	767 (12)
C(15)	4018 (5)	4528 (5)	−3067 (6)	1170 (16)
B	987 (4)	2909 (3)	−1725 (5)	512 (10)

Table 2. *Bond lengths (Å), $P\bar{1}$ refinement*

Cu—N(1)	2·142 (3)	B—N(2)	1·522 (5)	C(2)—C(1)	1·488 (6)
Cu—N(3)	2·020 (2)	B—N(4)	1·539 (5)	C(7)—C(6)	1·504 (5)
Cu—N(5)	2·284 (3)	B—N(6)	1·534 (5)	C(12)—C(11)	1·510 (7)
N(1)—N(2)	1·384 (4)	N(1)—C(2)	1·330 (5)	C(2)—C(3)	1·389 (6)
N(3)—N(4)	1·380 (4)	N(3)—C(7)	1·336 (4)	C(7)—C(8)	1·386 (5)
N(5)—N(6)	1·374 (4)	N(5)—C(12)	1·344 (5)	C(12)—C(13)	1·375 (7)
N(2)—C(4)	1·359 (5)	C(3)—C(4)	1·361 (6)	C(4)—C(5)	1·506 (6)
N(4)—C(9)	1·352 (4)	C(8)—C(9)	1·364 (5)	C(9)—C(10)	1·496 (5)
N(6)—C(14)	1·349 (5)	C(13)—C(14)	1·362 (6)	C(14)—C(15)	1·498 (7)

Coordinates of the C, N, and B atoms are given in Table 1.* Difference maps in the planes of the methyl hydrogen atoms suggested that these groups are disordered, and they were represented by six half-populated sites with C—H = 0·95 Å; after unsatisfactory attempts to refine the coordinates of the remaining four H atoms, these were placed in idealized positions with C—H = 1·0, B—H = 1·1 Å. Bond lengths for the $P\bar{1}$ structure are given in Table 2. The Cu atom now lies at a center of symmetry and the two HB(3,5-Me₂pz)₃ ligands are equivalent by symmetry; within each ligand there is no discernible difference between corresponding bond lengths in the three pyrazole rings. However, there are large differences among the three Cu—N bond lengths; the coordination about Cu is best described as 2 + 2 + 2 rather than the more usual 4 + 2 (or 4 + 1). There appears to be little correlation between the Cu—N distance and other bond lengths within the ligand; however, all three pyrazole rings are distorted as a result of the strength of the N—B bond compared to N—Cu (see Fig. 1).
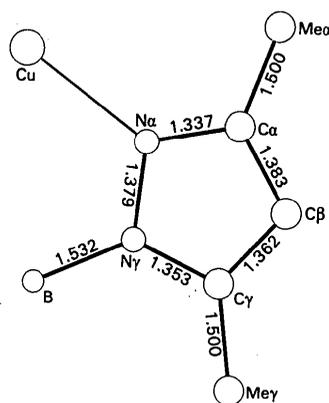

Fig. 1. Average bond lengths within the dimethylpyrazole groups. Except for the Cu—N distances, values for the three rings within each ligand agree approximately within the e.s.d.'s (see Table 2). The e.s.d.'s in the *average* values are about 0·003–0·004 Å.

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* Coordinates of the H atoms, U_{ij}'s of the heavier atoms, and a listing of observed and calculated structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51731 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structure of ErFe(CN)₆.4H₂O. Corrigendum.

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Abstract

The crystal structure of the title compound has been described as monoclinic, space group $P2_1/m$, with $a = 7·431$ (1), $b = 13·729$ (2), $c = 7·435$ (2) Å, $\beta = 120·02$ (2)°, $Z = 2$ [Mullica, Perkins, Sappenfield & Leschnitzer (1989). *Acta Cryst.* C**45**, 330–331.] It should be described as orthorhombic, space group *Cmcm*, with $a = 7·435$, $b = 12·868$, $c = 13·729$ Å, $Z = 4$. Revised coordinates are given.

The vectors defining the new cell edges are [00$\bar{1}$], [$\bar{2}$0$\bar{1}$], and [010]; the corresponding coordinate transformations are $x' = (x/2) - z$, $y' = -(x/2)$, $z' = y$. After averaging the transformed coordinates over appropriate pairs of atoms, the *Cmcm* coordinates in Table 1 result. No atom needed to be shifted as much as its reported e.s.d. [Mullica, Perkins, Sappenfield & Leschnitzer (1989) (hereafter MPSL), Table 1] in order to comply with the symmetry of *Cmcm*. Thus, there are no significant changes in the bond lengths or angles (MPSL, Table 2).

Table 1. *Coordinates, space group* Cmcm

	Site	x	y	z
Er	4(c)	0·50	−0·17647	0·25
Fe	4(a)	0·00	0·00	0·50
C(1,3)	16(h)	0·1844	−0·0466	0·4110
C(2)	8(f)	0·00	−0·1362	0·5596
N(1,3)	16(h)	0·2965	−0·0756	0·3608
N(2)	8(f)	0·00	−0·2160	0·5964
O(1)	8(f)	0·50	0·1553	0·4001
O(2,3)	8(g)	0·265	0·215	0·25

As MPSL note, the compound is isotypic with BiFe(CN)₆. Interestingly, however, this latter compound was also first reported as monoclinic, space group $P2_1/m$, but with a different choice of axes (Mullica, Perkins & Sapperfield, 1988), and also had its space group revised to *Cmcm* (Marsh, 1989).

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