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**On the crystal structure of bis(dipicolinato)ferrate(III) dihydrate.** By RICHARD E. MARSH, *The Beckman Institute,\* California Institute of Technology, Pasadena, California 91125, USA*

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**Abstract**

The structure of  $[\text{H}_5\text{O}_2]^+[\text{Fe}(\text{C}_7\text{H}_3\text{NO}_4)_2]^-$  was recently described and refined [Cousson, Nectoux & Rizkalla (1992). *Acta Cryst.* **C48**, 1354–1357] in space group *Pnn2* [orthorhombic,  $a = 8.860$  (8),  $b = 11.007$  (2),  $c = 16.316$  (4) Å,  $Z = 4$ ]; it is better described in *Pnna*. Revised coordinates are given.

Coordinates in space group *Pnna* were obtained from those in Table 1 of Cousson *et al.* (1992) by incrementing  $x$  by 0.25, decrementing  $z$  by about 0.227, and averaging over equivalent atoms in the two molecules. Refinement by full-matrix least squares was based on 1554  $F_{\text{obs}}$  values recovered from SUP 54982; the quantity minimized was  $\sum w(F_{\text{obs}}^2 - F_{\text{calc}}^2)^2$ , with weights  $w$  assigned according to Hughes (1941). At convergence [ $(\Delta/\sigma)_{\text{max}} = 0.04$ ]  $R$  was 0.041 for 148 parameters {coordinates of all atoms;  $U_{ij}$  values for Fe, C, N and O atoms; isotropic  $B$  values for H atoms; scale factor [final value 0.988 (2)]; and extinction coefficient [ $0.79$  (6)  $\times 10^{-6}$ ]}. For the earlier *Pnn2* model, Cousson *et al.* (1992) also reported an  $R$  value of 0.041, for 251 parameters. Included in SUP 54982 were 12 reflections of the type  $hk0$  with  $h$  odd, which are forbidden in *Pnna*. All were extremely weak, with  $F_{\text{obs}}$  values that obviously were close to the 'unobserved' cut-off of  $I \leq 3\sigma(I)$  (Cousson *et al.*, 1992). Their presence, if real, can surely be blamed on the Renninger effect.

Final *Pnna* coordinates for the heavy atoms are given in Table 1.† Changes from the *Pnn2* coordinates range up to 0.12 Å – highly significant in view of the e.s.d.'s of 0.005 Å or less. Most of the general features of the structure remain unchanged; in particular, the inequalities in the Fe–N [2.071 (3), 2.034 (3) Å] and Fe–O [2.004 (2), 2.038 (2) Å]

\* Contribution No. 8752.

† Lists of structure factors,  $U_{ij}$  values, coordinates and  $B$  values for the H atoms, and bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55678 (9 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: BU0317]

Table 1. Coordinates ( $\times 10^4$ ) and  $U_{\text{eq}}$  values ( $\text{Å}^2 \times 10^4$ ), space group *Pnna*

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_j.$$

	$x$	$y$	$z$	$U_{\text{eq}}$
Fe	2500	0	3114 (4)	331 (1)
C(1)	1044 (4)	–1726 (3)	4171 (2)	388 (7)
C(2)	1774 (3)	–877 (3)	4774 (2)	338 (6)
C(3)	1745 (4)	–903 (4)	5619 (2)	448 (8)
C(4)	2500	0	6036 (3)	504 (12)
C(5)	4803 (3)	–998 (3)	2057 (2)	378 (7)
C(6)	3622 (3)	–533 (3)	1471 (2)	290 (6)
C(7)	3649 (4)	–576 (3)	629 (2)	408 (7)
C(8)	2500	0	205 (3)	490 (12)
N(1)	2500	0	4383 (2)	314 (7)
N(2)	2500	0	1867 (2)	261 (6)
O(1)	1359 (3)	–1505 (2)	3420 (1)	470 (6)
O(2)	209 (3)	–2553 (3)	4402 (2)	559 (6)
O(3)	4437 (3)	–891 (2)	2811 (2)	449 (5)
O(4)	5990 (3)	–1389 (3)	1774 (2)	625 (8)
O(W)	–1150 (3)	–3298 (3)	3021 (2)	531 (7)

bond lengths to the two picolinate dianions, noted by Cousson *et al.* (1992), become even more significant. However, contrary to the results of Cousson *et al.* (1992) the carboxylate groups in these two dianions now look to have matching C–O bond lengths, at 1.279 (3) Å to the Fe-coordinated O atoms and 1.229 (3) Å to the others (which accept strong hydrogen bonds from the  $\text{H}_5\text{O}_2^+$  cation); there is no indication of equal C–O distances and, hence, 'equal distribution of charge on both O atoms' in either carboxylate group. The central O...O bond in the  $\text{H}_5\text{O}_2^+$  group, which lies across a crystallographic twofold axis, is short at 2.444 (6) Å – a distance suggestive of a symmetric O–H–O bond. Attempts to refine the central H atom either as disordered between two sites on opposite sides of the  $C_2$  axis or as a single anisotropic atom lying on the  $C_2$  axis were inconclusive; in the final refinement cycles it was modeled as ordered and isotropic [ $B = 16$  (4) Å<sup>2</sup>], on the  $C_2$  axis.

**References**

- COUSSON, A., NECTOUX, F. & RIZKALLA, E. N. (1992). *Acta Cryst.* **C48**, 1354–1357.  
 HUGHES, E. W. (1941). *J. Am. Chem. Soc.* **63**, 1737–1752.

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