Confirmation of Monoclinic $BiFe(CN)_6 \cdot 4H_2O$*

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This letter is a rebuttal to the article entitled 'Three Incorrect Space Groups' in *Inorganica Chimica Acta*, Volume 142 [1]. It is true that there are four misprints in Table I of the paper in question [2]. However, these inadvertent misprints would be obvious to anyone using the atomic coordinates to reproduce bond distances and angles. After applying the appropriate transformation to the reduced data, intensity discrepancies were still observed as stated in the original paper in question [2]. Nevertheless, the data were again averaged ($R_{int} = 0.058$) and refined using a full-matrix least-squares program. The residual index values (once again) were $R = 0.049$ and $R_w = 0.062$ with a 'goodness of fit' (Σ_2) equal to 2.34 (see Table 1 for a comparison).

After comparing the results of both refinements (as was done before publishing the original paper in question), it was deemed necessary that a statistical significance test be administered. According to Hamilton [3], the *Cmcm* model is not significantly better than $P2_1/m$. The hypothesis (H_0) that the more restricted centric space group (*Cmcm*) is the correct space group rather than the less restricted centric space group ($P2_1/m$), which is the alternate hypothesis (H_a), was tested. The ratio [$R(Cmcm)/R(P2_1/m)$] was much much greater than the Hamilton $\mathcal{R}$ at the 0.005 significance level. Consequently, the null hypothesis (H_0) was strongly rejected and the alternate hypothesis (H_a) was accepted. $P2_1/m$ is the correct space group.

One can say that the higher symmetry space group should be chosen. If this be the case, one should pick an even higher choice, *i.e.*, the hexagonal $P6_3/m$. The data yield R values of 0.082 and 0.096 in this space group. Further crystallographic results should be internally consistent. The resultant average C≡N bond distance obtained from the *Cmcm* model is 1.126 Å (1.143 and 1.11 Å) which is quite reasonable. However, the average C≡N bond distance obtained from the $P2_1/m$ model is 1.141 Å (1.153, 1.134 and 1.137) which is directly in line with the summation of radii obtained from the work of Shannon [4] and in very good agreement with experimental literature values found in BIDICS [5]. Finally, it was stated [1] that $BiFe(CN)_6 \cdot 4H_2O$ was indeed isomorphous with the lanthanide compounds $LnCo(CN)_6 \cdot 4H_2O$ described by Hulliger *et al.* [6, 7]. These authors [6, 7] also described $LnFe(CN)_6 \cdot 4H_2O$ compounds as being isomorphous to the $LnCo(CN)_6 \cdot 4H_2O$, *i.e.*, in the orthorhombic space group *Cmcm* [8]. Hulliger *et al.* [8] gave single crystals of $SmFe(CN)_6 \cdot 4H_2O$ to Kietaible and Petter [9]. This group [9] published a very brief report (only lattice constants and $Z = 4$ were reported, no crystallographic data) which confirmed the X-ray powder results of Hulliger *et al.* [6–8]. However, no complete structural analysis has ever followed the report.

TABLE 1. Comparative Results

Space group	$P2_1/m$	*Cmcm*
Z	2	4
R_{int}	0.020	0.058
R	0.030	0.049
R_w	0.031	0.062
Variables	91	49
Unique data	1036	602
Σ_2	1.68	2.34

Extensive contemplation and investigation led to the conclusion that $BiFe(CN)_6 \cdot 4H_2O$ crystallizes in space group $P2_1/m$. This conclusion was not arrived at without much thought to the work of Hulliger *et al.* [6–8] and was not arrived at by merely reviewing their experimental work, but rather by extensive experimentation in the laboratory using every available method. We are far from being infallible and until future experimentation presents better results related to $BiFe(CN)_6 \cdot 4H_2O$ and its analogs, we stand by our conclusions.

Acknowledgement

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