Supporting information for:

Pitfalls in Metal-Organic Framework Crystallography: Towards More Accurate Crystal Structures

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Determination of the twin law in NU-1100

During space group determination (with e.g. XPREP), initial analysis of the reflection intensities from NU-1100 (as obtained from CSD entry number 983542[1]) indicate the space group to be Im-3m.

Output from XPREP:

```
Original cell in Angstroms and degrees:

   44.026   44.026   44.026    90.00    90.00    90.00

  113919 Reflections read from file n2807_a.hkl; mean (I/sigma) =    6.97
------------------------------------------------------------------------------
Search for higher metric symmetry
Identical indices and Friedel opposites combined before calculating R(sym)
------------------------------------------------------------------------------
Option A: FOM = 0.000 deg.   CUBIC        I-lattice   R(sym) = 0.046 [  80218]
Cell:   44.026  44.026  44.026   90.00   90.00   90.00    Volume:     85335.08
Matrix: 1.0000  0.0000  0.0000  0.0000  1.0000  0.0000  0.0000  0.0000  1.0000

Option A selected
------------------------------------------------------------------------------
Lattice exceptions:  P      A      B      C      I      F     Obv    Rev    All

N (total) =          0  56920  57009  56981      0  85455  75936  75979 113919
N (int>3sigma) =     0  26858  27240  27038      0  40568  42730  42819  64208
Mean intensity =   0.0    9.3    9.5    9.6    0.0    9.4   35.4   35.2   35.6
Mean int/sigma =   0.0    4.5    4.6    4.5    0.0    4.5    7.0    7.0    7.0

Crystal system C and Lattice type I selected
Mean |E*E-1| = 1.181 [expected .968 centrosym and .736 non-centrosym]

Systematic absence exceptions:
        41/43  a--    --d

N        39   2684   3714
N I>3s   37   1879   1807
<I>    1463   24.4  144.5
<I/s>  23.7    7.9    9.3

Identical indices and Friedel opposites combined before calculating R(sym)

Option  Space Group  No.  Type  Axes  CSD  R(sym) N(eq)  Syst. Abs.   CFOM

[A] Im-3           #204  centro   1     4  0.046  80218  0.0 /  7.0  27.58
[B] I23            #197  chiral   1     4  0.046  80218  0.0 /  7.0  42.83
[C] I2(1)3         #199  chiral   1     1  0.046  80218  0.0 /  7.0  72.83
[D] Im-3m          #229  centro   1    20  0.048  86392  0.0 /  7.0  10.71
[E] I-43m          #217  non-cen  1    19  0.048  86392  0.0 /  7.0  26.20
[F] I432           #211  chiral   1     0  0.048  86392  0.0 /  7.0 121.20

Option [D] chosen
```

Based on systematic absences and R(sym), XPREP cannot distinguish which the coorect space group is. A non-twinned crystal in space group Im-3 would have given a large R(sym) value for space group Im-3m, but the twinning obscures this. The only indication we have that there may be twinning is the elevated value of `|E*E-1|`.

However, no satisfactory structure can be obtained in space group Im-3m. When working with high-symmetry structures, data should be checked for twinning by merohedry. Output from XPREP:

```
Comparing true/apparent Laue groups.  0.05 < BASF < 0.45 indicates partial
merohedral twinning.  BASF ca. 0.5 and a low <|E^2-1|> (0.968[C] or 0.736[NC}
are normal) suggests perfect merohedral twinning.  For a twin, R(int) should be
low for the true Laue group and low/medium for the apparent Laue group.


 [1] m-3 / m-3m: R(int) 0.052(100717)/0.015(6174), <|E^2-1|> 1.147/1.157
 TWIN  0 1 0  1 0 0  0 0 -1
   BASF  0.441 [C]  or  0.425 [NC]
```

XPREP finds the correct twin law and Laue class, which may be used for proper structure determination.

Another approach is to use the tables for space group determination by Howard Flack.[2] When the apparent space group is located, the other possible combinations of space group and twin operators are shown in the same section of the table:

Observed Laue class $m\ \bar{3}m$
Observed crystal class $m\ \bar{3}m$

-- Reflection conditions ----------

hkl	0*kl*	*h*0*l*	*hk*0	*[…]*	*h*00	0*k*0	00*l*	Space group
h + *k* + *l*	*k* + *l*	*h* + *l*	*h* + *k*		*h*	*k*	*l*	*Im* $\bar{3}m$ (229)
								γ *Im* $\bar{3}$ (204)
								T_t *I*4/*m* (87)
								T_t *I*4_1/*a* (88)
								T_t *I*4*mm* (107)
								T_t *I*4*cm* (108)
								T_t *I*4_1*md* (109)
								T_t *I*4_1*cd* (110)
								T_t *I*4/*mmm* (139)
								T_t *I*4/*mcm* (140)
								T_t *I*4_1/*amd* (141)
								T_j *R* $\bar{3}$ (148)
								T_j *R* $\bar{3}m$ (166)
								T_j *R* $\bar{3}c$ (167)

γ = twin by $2_{[110]}$

Again, the correct description can be found (space group *Im* $\bar{3}$ twinned by $2_{[110]}$). The other options in the list are combinations of unit cells with special metrics and twin operators.

The structure is then determined by solving the structure in the correct lower-symmetry space group, and then applying the twin law in the structure refinement. For good examples and procedures see the texts by Herbst-Irmer and coworkers.[3, 4]

1. O. V. Gutov, W. Bury, D. A. Gomez-Gualdron, V. Krungleviciute, D. Fairen-Jimenez, J. E. Mondloch, A. A. Sarjeant, S. S. Al-Juaid, R. Q. Snurr, J. T. Hupp, T. Yildirim and O. K. Farha, *Chem.-Eur. J.*, 2014, **20**, 12389-12393.
2. H. Flack, *Acta Crystallogr. Sect. C*, 2015, **71**, 916-920.
3. R. Herbst-Irmer, in *Crystal Structure Refinement*, ed. P. Müller, Oxford Science Publications, Oxford, 2006, ch. 7, pp. 106-149.
4. I. Guzei, R. Herbst-Irmer, A. Munyaneza and J. Darkwa, *Acta Crystallogr. Sect. B*, 2012, **68**, 150-157.