An example of the refinement of positional disorder modeled as compositional disorder in [5-(2-formylphenyl)-10,15,20-triphenylporphyrinato]nickel(II)

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The title compound, [Ni($C_{45}H_{28}N_4O$)], crystallizes in the space group $I\bar{4}2d$ and resides on a crystallographic fourfold rotoinversion axis with only a quarter of the complex in the asymmetric unit. The complex displays positional disorder as the one aldehyde group on the ligand can be located at four different positions. It was necessary to model this as compositional disorder to obtain a correct model and refinement. The practical approach to the refinement is explained.

Comment

Metalloporphyrin complexes and metalloporphyrin assemblies are of longstanding interest in biological systems, where they are widely used as active sites or cofactors in various enzymes to store redox equivalents, transport dioxygen, to collect solar energy and to activate small molecules (Behar *et al.*, 1998; Morris *et al.*, 2009; Naruta & Sasaki, 1994; Shimazaki *et al.*, 2004; Collman *et al.*, 2007). One of the recent advances in the field is the utilization of 1,2-phenylene-bridged bismanganese diporphyrin as a water oxidation catalyst (Shimazaki *et al.*, 2004). The unsymmetrical free-base 5-(2-formylphenyl)-10,15,20-triphenylporphyrin (H_2TPP-CHO) is an important intermediate in the synthesis of this catalyst. Metallation of H_2TPP-CHO by nickel acetate (Yao *et al.*, 2012) yielded [5-(2-formylphenyl)-10,15,20-triphenylporphyrinato]nickel(II), (I), a potentially useful precursor for the synthesis of hetero-bimetallic diporphyrins.

The structure of (I) based on the synthetic procedure and spectroscopic evidence is shown in the Scheme. The Ni complex occupies the crystallographic fourfold rotoinversion axis (Wyckoff position *a*); thus only a quarter of the complex is symmetry independent (Fig. 1). There must be disorder in this crystal structure because the complex lacks any symmetry

except for the identity (theoretically C_S is possible). The aldehyde group is therefore required to be disordered over four positions in the structure. In the asymmetric unit, this disorder manifests itself by having an occupancy of 25% for the aldehyde group, whereas the other 75% of the time a H atom must reside in its place.

A search of the IUCr journals for other similar examples of disorder modeling using the search terms 'positional disorder' and 'compositional disorder' yielded only one other relevant paper (Guzei *et al.*, 2008). While this paper reports positional disorder modeled as compositional disorder similar to that in (I), it does not outline the procedure for such modeling. Therefore we will briefly describe a suitable disorder handling procedure for (I) using the program *SHELXL97* (Sheldrick, 2008).

(I)
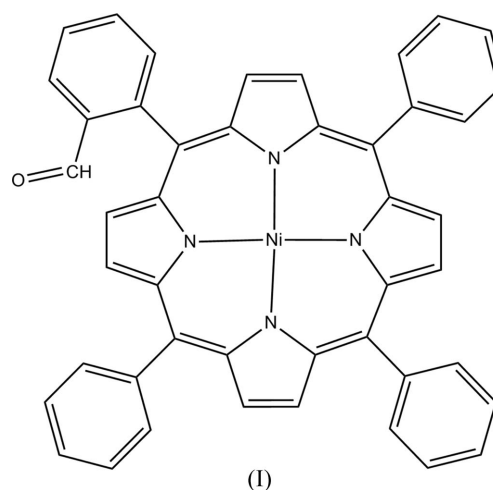
The procedure is not difficult if one knows what needs to be done and what facilities *SHELXL97* offers. First of all, the 3:1 ratio of the H-to-aldehyde group was known *a priori*. After the routine structure solution and straightforward refinement of atoms Ni1, N1, N2 and C1–C11, one must locate the partially occupied (occupancy of 0.25) aldehyde group and partially present (occupancy of 0.75) H atom on atom C11.
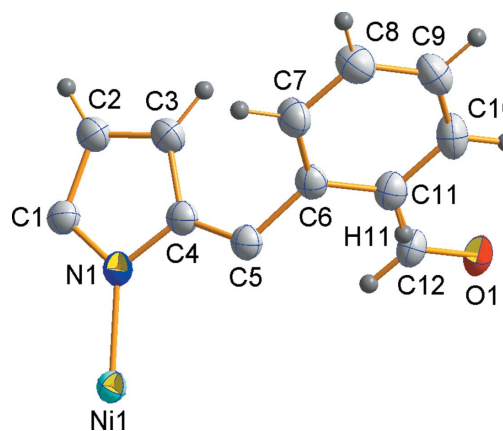

Figure 1
The structure of the asymmetric unit of (I), with both parts of the disordered atoms shown. The displacement ellipsoids are shown at the 50% probability level.

metal-organic compounds

When multiplied by 4, these occupancies produce the correct molecular composition. There were two peaks of residual electron density (*ca* 2 e Å^{-3}) near atom C11, and they were identified and labeled as C12 and O1. Option PART of the program *SHELXL* was used to separate the partially occupied moieties and prevent the program from considering that they are bonded to each other. The instruction file was manually edited as follows:

```
C11 1 0.68614 0.60979 0.58742 11.00000 0.04948
PART 1
AFIX 43
H11 2 0 0 0 10.75 −1.2
AFIX 0
PART 2 10.25
HFIX 43 −1.2 C12
C12 1 0.74510 0.61110 0.50400 11.00000 0.05
O1 4 0.73520 0.63160 0.41710 11.00000 0.05
PART 0
```

Atom H11 belongs to PART 1, whereas atoms C12 and O1 belong to PART 2. The use of two different PARTs was necessary in order to help the program place the H atoms at the correct positions at atoms C11 and C12. Atoms specified in PART 1 and PART 2 are not present simultaneously at any one location in the structure and cannot (and should not, *vide infra*) be chemically bonded. Atom H11 is input with dummy coordinates of 0,0,0, and command AFIX 43 which ensures the correct placement of the atom on C11 at an idealized position. The correct coordinates for H11 will be generated by the program. For all atoms in PART 2 the occupancy is assigned

on the PART line with the second parameter. The first parameter designates the PART number, the second the occupancy. In PART 2, the first command is HFIX 43 −1.2 C12, which will generate the aldehyde H atom for C12 in an idealized position. These ten lines of instructions as given above completely address the disorder, but of course other approaches are possible. After another set of 12 cycles of least-squares, the non-H atoms were refined anisotropically and a chemically reasonable and computationally stable refinement achieved.

The correct assignment of the occupancies of PART 1 and PART 2 can also be checked by refining the occupancy of the aldehyde group independently; indeed, it refines to 0.237 (5). As mentioned above, the correct molecular composition was confirmed by other analyses.

The final structure is presented in Fig. 2. Only one of the four possible positions of the aldehyde group is shown to display the correct chemical composition. Aside from the disorder and its facile modeling, this structure is unexceptional with typical geometrical parameters as comfirmed by a *Mogul* structural check (Bruno *et al.*, 2002). The porphyrinate ligand is saddle shaped, consistent with its $\overline{4}$ symmetry. The C5—Ni1—C5($-x + 2$, $-y + 1$, z) angle is 162.59 (8)°, atom C5 and its symmetry mates alternatively reside 0.512 (2) Å below and above the best least-squares plane defined by them. It should be noted that for this structure some visualization and data validation programs indicate the presence of conflicting close contacts between symmetry-related O atoms of the aldehyde groups. It is important to keep in mind that the observed structure is the average structure and that the fourfold symmetry of the average structure puts the minor aldehyde components at four different positions in the crystal. In each molecule, there is only one aldehyde group, thus any close 'contact' between such symmetry-related aldehyde groups is not real because each group is occupied only 25% of the time. When the aldehyde group is present at one site in any particular molecule in the crystal, it is not present at a conflicting nearby site in the neighboring molecule. In general, such 'false contacts' are not a concern if the total occupancy of the 'conflicting' atoms does not exceed unity. Nonetheless, visualization and validation software are sometimes unable to appropriately recognize such situations and may produce false indications of close contacts or draw a spurious chemical bond between would-be conflicting atoms. The user should remain aware of the real situation at the local level of the structure.

Although the disorder in this structure is technically positional, it was necessary to model it as compositional owing to the symmetry considerations: only a quarter of the Ni complex is symmetry independent, and two groups appear to share the same site.
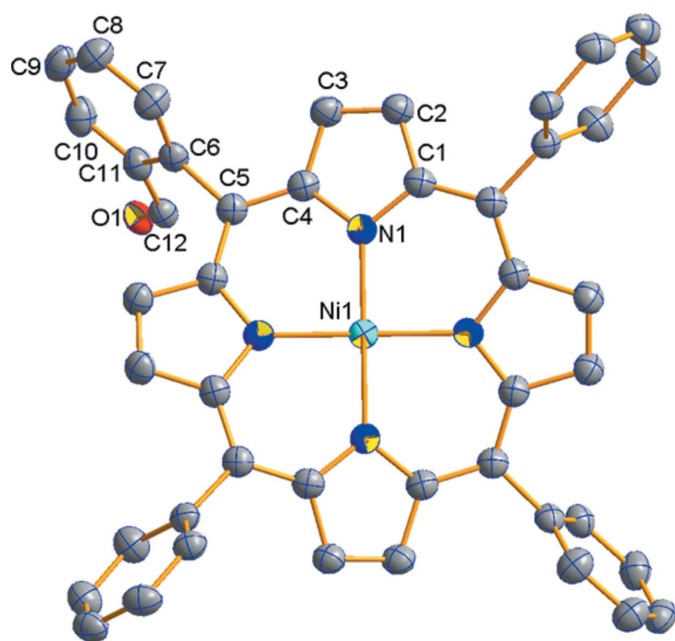

Figure 2
The molecular structure of (I), with displacement ellipsoids shown at the 50% probability level. All H atoms have been omitted for clarity. The aldehyde group is only shown in one of the four possible positions which are each occupied 25% of the time.

Experimental

All the solvents, *viz.* chlorobenzene, chloroform, dimethylformamide (DMF) and heptanes, were purchased from Sigma–Aldrich. Nickel acetate and sodium acetate were also purchased from Sigma–Aldrich. The free-base porphyrin 5-(2-formylphenyl)-10,15,20-triphenylpor-

phyrin was prepared according to a previously published procedure (Ye & Naruta, 2003).

The title nickel–porphyrin complex, (I), was prepared in a similar manner to methods described previously (Yao *et al.*, 2012). Under ambient atmospheric conditions, in a 100 ml distillation flask, 5-(2-formylphenyl)-10,15,20-triphenylporphyrin (170 mg, 0.26 mmol) and NaOAc (20 mg, 0.63 mmol) were stirred in a 3:1 (*v/v*) chlorobenzene–DMF solvent mixture (50 ml). After the addition of 8 equivalents of $Ni(OAc)_2 \cdot 4H_2O$ (440 mg, 1.28 mmol), a Soxhlet extractor with a cellulose filter thimble filled with 3 g of K_2CO_3 was attached to the distillation flask. The assembly was completed with a condenser at the top of the extractor; the mixture was then heated under reflux at 423.15 K overnight. The reaction progress was monitored by thin-layer chromatography until all the H_2TPP was consumed. After the reaction was complete, the solvent was removed under vacuum. The remaining solid was dissolved in chloroform (150 ml) and washed with water (5 × 20 ml). The organic layer was further washed with a saturated sodium bicarbonate solution (3 × 20 ml) and dried over K_2SO_4. After removal of the solvent *in vacuo*, bright orange solids were collected (yield: 76.5%, 123 mg, 0.18 mmol). MS (MALDI-anthracene) *m/z* (%): 699 (100) $[M + H]^+$. H NMR (300 MHz, CDCl₃): δ 9.34 [*s*, 1H, C(H)O], 8.74 (*s*, 6H, β-pyrrole), 8.54 (*s*, 1H, β-pyrrole), 8.55 (*s*, 1H, β-pyrrole), 8.35 (*m*, 1H, *o*-phenyl), 8.13 (*m*, 1H, *p*-phenyl), 7.69 (broad, 6H, *o*-phenyl), 7.85 (*m*, 2H, *m*-phenyl), 7.69 (broad, 9H, *m*- and *p*-phenyl). UV–vis (CH₂Cl₂) λ_{max}(nm): 415 (Soret), 530. About 10 mg of bright orange solid was dissolved in chloroform, which was layered with excess heptane. The recrystallization tube was stored at room temperature. Orange crystals suitable for single-crystal X-ray diffraction studies were isolated after two weeks.

Crystal data

[Ni(C₄₅H₂₈N₄O)]
$M_r = 699.42$
Tetragonal, $I\overline{4}2d$
$a = 15.6514 (5)$ Å
$c = 13.0600 (4)$ Å
$V = 3199.26 (17)$ Å³

$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.65$ mm⁻¹
$T = 100$ K
$0.09 \times 0.08 \times 0.07$ mm

Data collection

Bruker SMART APEXII
area-detector diffractometer
Absorption correction: analytical
(*SADABS*; Bruker, 2009)
$T_{min} = 0.944$, $T_{max} = 0.958$

33791 measured reflections
1989 independent reflections
1865 reflections with $I > 2\sigma(I)$
$R_{int} = 0.047$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.080$
$S = 1.16$
1989 reflections
130 parameters
H-atom parameters constrained

$\Delta\rho_{max} = 0.19$ e Å⁻³
$\Delta\rho_{min} = -0.21$ e Å⁻³
Absolute structure: Flack (1983), 781 Friedel pairs
Flack parameter: 0.000 (19)

Table 1
Selected geometric parameters (Å, °).

Ni1—N1ⁱ	1.9259 (17)		
N1ⁱ—Ni1—N1ⁱⁱ	90.001 (1)	N1ⁱⁱ—Ni1—N1	179.55 (12)

Symmetry codes: (i) $-y + \frac{3}{2}, x - \frac{1}{2}, -z + \frac{3}{2}$; (ii) $-x + 2, -y + 1, z$.

H atoms attached to C atoms were placed in idealized locations and refined as riding with appropriate displacement parameters of $U_{iso}(H) = 1.2U_{eq}$(parent atom). Default effective X—H distances for $T = 100$ K were Csp^2—H = 0.95 Å.

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT-Plus* (Bruker, 2009); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*, *OLEX2* (Dolomanov *et al.*, 2009), *FCF_filter* (Guzei, 2007) and *INSerter* (Guzei, 2007); molecular graphics: *SHELXTL* and *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *SHELXTL*, *publCIF* (Westrip, 2010) and *modiCIFer* (Guzei, 2007).

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