Correction of the space group of [Ni(bipy)$_2$(ONO$_2$)$_2$]·2(pyrene)

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The crystal structure of [Ni(bipy)$_2$(ONO$_2$)$_2$]·2(pyrene), poly[[[bis(nitrato-*O*)nickel(II)]bis(μ-4,4′-bipyridyl-*N,N*′] bis-(pyrene)], was originally reported in space group *Pn* [Biradha *et al.* (1999). *Chem. Commun.* pp. 1327–1328]. Reasons are given for changing the space group to *P*2$_1$/*n*. Consequently, incorrect descriptions of the title compound in the literature must be altered. In particular, the structure is not polar. It is further contended that description in terms of 'complementary, interpenetrating covalent and noncovalent two-dimensional networks' is misleading as the 'noncovalent network' (of pyrenes) has geometrical but not physical significance. The title compound is a typical host–guest inclusion complex.

Incorrect assignment of a space group in determination of a crystal structure can have a variety of consequences; many examples are given by Marsh *et al.* (2001), and earlier papers cited therein). Here we show that the assignment of space group *Pn* to [Ni(bipy)$_2$(ONO$_2$)$_2$]·2(pyrene) (bipy = 4,4′-bipyridine; Biradha *et al.*, 1999) was wrong and note the changes required by revision to *P*2$_1$/*n*.

This structure [a = 11.3602 (6), b = 22.771 (1), c = 15.8580 (9) Å, β = 93.956 (1)°, Z = 4] was determined using 14 277 reflections out of 15 136 unique reflections (4 < 2θ < 56°) measured at 200 K on a Siemens SMART CCD diffractometer with Mo *K*α radiation; θ scan mode; the highest (residual) electron density peak and hole were 0.75 and −0.66 e Å^{-3}. Space groups *Pn* (No. 7) and *P*2/*n* (No.13) are compatible with the *reported* reflection conditions; an ordered structure in *Pn* was successfully refined (1172 parameters, R_1 = 0.041, wR_2 = 0.103; H atoms in calculated positions, all other atoms refined anisotropically), while a model based on disordered pyrenes was tried, and rejected. It is not clear whether refinement in *P*2/*n* was considered.

The title complex is one member of an extended family of isostructural complexes based on [M(4,4′-bipy)$_2X_2$] and similar nets; among examples within the immediate family are [Co(bipy)$_2$(NCS)$_2$]·2(Et$_2$O) (Lu *et al.*, 1997; RINPUZ), [Cd(bipy)$_2$(ONO$_2$)$_2$]·2(*o*-C$_6$H$_4$Br$_2$) (Fujita *et al.*, 1994; YECFAN), [Cd(bipy)$_2$(ONO$_2$)$_2$]·2(*o*-nitroaniline) (Huang *et al.*, 1999) and [Cd(bipy)$_2$(NO$_3$)$_2$]·4(H$_2$O) (Aoyagi *et al.*, 2000). The structures can be described in a similar way (Fig. 1). The 4,4′-bipyridine ligands link the metal atoms in an approximately square net,[1] approximately 11.5 Å on edge, repeating to give a two-dimensional layer (or net) of composition $^{\infty}_2[M(\text{bipy})_{4/2}]$. The other ligands (ONO$_2$ anions in the title complex) are coordinated to the metal atoms and extend

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[1] It is useful to follow Moulton & Zaworotko (2001) and distinguish between 'framework' and 'net'; framework refers to the construction of the structure as a whole, while net is used to describe two-dimensional layers.

above and below the layer. Successive layers are offset in different ways for each complex and the guest molecules are accommodated in the spaces between the layers. Each metal atom has six nearest neighbours in a quasi-octahedral *trans*-MN_4X_2 arrangement. In [Ni(bipy)$_2$(ONO$_2$)$_2$]·2(pyrene) the four N atoms (of the bipy ligands) and two O atoms (of the nitrates) form slightly compressed octahedra about the Ni centres {mean d(Ni—N) = 2.131 (5) [18] Å, mean d(Ni—O) = 2.094 (5) [19] Å}.[2] The octahedron deviates from a regular form, the largest deviation from 90 or 180° of angles subtended at Ni being 10°.

With Z = 4 and space group *Pn*, there are two crystallographically independent formula units in the unit cell. Two criteria suggest that space group *Pn* is incorrect. The first is based on the separation of corresponding atoms of the two purportedly independent formula units along [010]. We illustrate this with respect to Ni1 and Ni2, which are separated by 0.49991 (*i.e.* 1/2) along [010]; similar results are obtained for other pairs of atoms. This eliminates *P2/n* as a possible space group, but shows that the correct space group has a twofold screw axis along [010], implying the space group *P2$_1$/n* (No. 14). The second is based on the spread of values of chemically equivalent geometrical parameters. The values of d(C—C) and d(C—N) in the bipy rings range from 1.321 (9) to 1.463 (9) Å (mean 1.39 [4]) and from 1.279 (8) to 1.399 (8) Å (mean 1.34 [5]), respectively; the values of d(C—C) between the rings range from 1.453 (9) to 1.517 (9) Å (mean 1.48 [3]). The values of d(N—O) in the nitrate ions range from 1.112 (8) to 1.392 (8) Å (mean 1.23 [9]), with the O—N—O angles ranging from 110.3 (7) to 136.5 (7)° (mean 120 [8]).[3]

The population s.u.s are therefore some three to ten times as large as the least-squares s.u.s. Such behaviour is typical of the situation where refinement of a centrosymmetric structure has been carried out in a non-centrosymmetric space group (Schomaker & Marsh, 1979).

We now address the question of how the arrangement described in *Pn* is transformed to *P2$_1$/n*.[4] There are three possible locations for inversion centres: at the Ni atoms, at the midpoints of the inter-ring bonds of the bipy ligands and at the midpoints of the central bonds of the pyrene molecules. Neither of the first two possibilities is supported by the structural results obtained in *Pn*: the immediate surroundings of the Ni atoms are not centrosymmetric, while the torsion angles about the four inter-ring bonds all differ significantly from 0°. There remain the midpoints of the central bonds of the pyrene molecules (C115—C116; C215—C216; C315—C316; C415—C416). These midpoints are separated from one another by combinations of 1/2 along the three axes. We move the midpoint of C115—C116 to 1/2, 1/2, 1/2 (this was an

arbitrary choice among the possibilities), *i.e.* the coordinates in *Pn* are corrected by Δx = −0.10315, Δy = −0.25, Δz = −0.3366.[5] The centres of the four pyrenes are located at Wyckoff positions (*a*), (*b*), (*c*) and (*d*) (PY1 at 0, 0, 0; 1/2, 1/2, 1/2; PY2 at 0, 0, 1/2; 1/2, 1/2, 0; PY3 at 0, 1/2, 0; 1/2, 0, 1/2; PY4 at 1/2, 0, 0; 0, 1/2, 1/2) of space group *P2$_1$/n*. The asymmmetric unit consists of one Ni, two (independent) bipyridines, two (independent) nitrates and four (independent) half-pyrenes, all at general positions in space group *P2$_1$/n*. Recognition of the arrangement in *P2$_1$/n* is made more difficult by pseudo-symmetries in the structure. For example, the pair of pyrenes PY1 and PY3 have similar, but not identical, orientations in the unit cell; the same holds for the pair of pyrenes PY2 and PY4 (Fig. 2). Indeed, Biradha *et al.* (1999) used this as evidence for the polar nature of the structure (see their Fig. 3 and accompanying text on p. 1328); the so-called polar nature of the structure has been mentioned on a number of occasions {see, for example, Biradha *et al.*, 2000, p. 3837}; [Ni(bipy)$_2$(ONO$_2$)$_2$]·2(pyrene) 'illustrates how polarity in crystals can be generated from subtle packing of achiral components, as illustrated by the presence of chiral networks of pyrene molecules' (see also p. 3841 of the same reference). The revised space group also explains why a Flack parameter (Flack & Bernardinelli, 1999, 2000) of 0.48 (2) was obtained in the refinement. The systematic absence '0k0 absent for k odd' appears to have been overlooked. This is perhaps the first crystal structure where all the special positions of a space group are occupied. Revised non-H atom coordinates are given in Table *A* (deposited and submitted to the CSD).[6]

The square covalently bonded net, typical (with minor variations) of all these structures, is shown in Fig. 1; this diagram, which is a (limited) projection on (001), has also been given by Biradha *et al.* (1999; see their Fig. 1*a*) and by others. Although such nets are often described as two-dimensional, this is an approximation as the nitrate groups protrude by ∼4 Å (z/4) above and below the plane of the Ni and N atoms. The adjacent net along [001] is obtained by the *n* glide operation, *i.e.* a shift of a/2 + c/2. The pyrene molecules are located about (002) planes in the spaces left between the superimposed, but shifted, nets. One must note that the covalent and (so-called) noncovalent nets shown in parts (*a*) (view down [001]) and (*b*) (view down [010]) of Fig. 1 of Biradha *et al.* (1999) are essentially mutually perpendicular, and cannot be directly superimposed. The two nets are correctly superimposed in their Fig. 2, viewed down [010]. Biradha *et al.* (1999) draw attention to 'weak CH···O hydrogen bonding between the 4,4′-bipy ligands and nitrate anions of the adjacent grids. C···O separations are in the range of 2.877–3.149 Å'. We have searched for these separations, but without success; our shortest separation is 3.04 Å (O3 to C21), but with an unfavourable geometry. Our shortest nitrate···pyrene O···C separation is 3.22 Å (O6 to C105),

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[2] The least-squares standard uncertainty is given in parentheses and the population standard deviation in square brackets.
[3] Owing to the inherent spread in the bond lengths of pyrene, we do not quote their variation.
[4] We quote from Biradha *et al.* (1999), 'Interestingly, although both nets appear centrosymmetric at first glance, the title compound crystallizes in the non-centrosymmetric space group *Pn* and is therefore polar. Pyrene molecules that lie opposite each other across the grid cavities in the *ac* plane are clearly not related by inversion and are therefore crystallographically nonequivalent'.

[5] In practice, the revised coordinates were obtained by an averaging process which took into account all symmetry-related pairs.
[6] Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM0042). Services for accessing these data are described at the back of the journal.
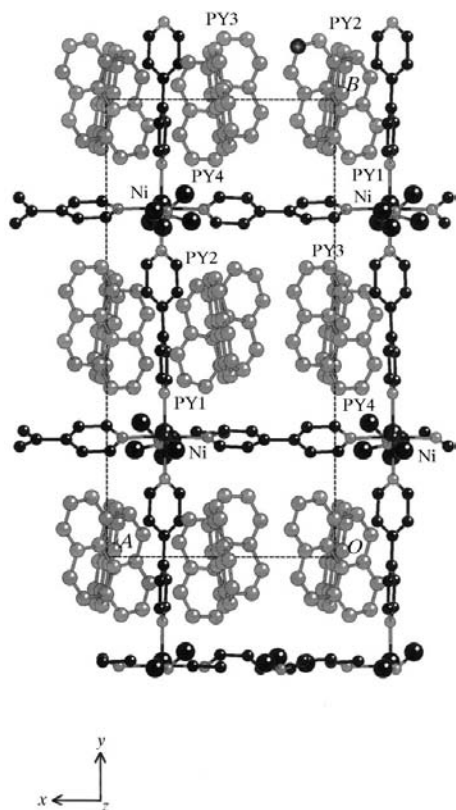
Figure 1
Projection of part of the structure onto (001). The single net shown is emphasized, with the 'cells' 11.5 Å on edge; the positions of the (obscured) Ni atoms are indicated. The largest circles are the O atoms of the nitrate groups, which protrude in both directions approximately perpendicular to the net plane. The next net is parallel to that shown, but shifted by the *n* glide. The pyrenes are enclathrated between the nets; PY1 and PY3 are somewhat inclined to (001), with PY2 and PY4 roughly perpendicular to this plane.

with a favourable geometry; this is probably to be identified with their 3.20 Å.

Biradha *et al.* (1999) have described [Ni(bipy)$_2$(O-NO$_2$)$_2$]·2(pyrene) as 'the first example of complementary, interpenetrating covalent and noncovalent two-dimensional networks', and 'are presently seeking other examples of compounds that contain complementary but chemically different nets'. It is meaningful to describe the [Ni(bipy)$_2$(ONO$_2$)$_2$] net as a physical entity because of the relatively strong covalent bonding between its three parts – Ni cations, neutral 4,4′-bipyridine ligands and anionic ONO$_2$ ligands. It would not be unreasonable to expect small 'rafts' of this composition to persist in solution. However, the noncovalent network of pyrenes is a purely geometrical concept, which is generated by the ordered repeating structure of the crystal; the pyrene molecules will be separate entities in solution. [Ni(bipy)$_2$(ONO$_2$)$_2$]·2(pyrene) is a typical example of a host–guest inclusion complex (Herbstein, 1993); the superimposed
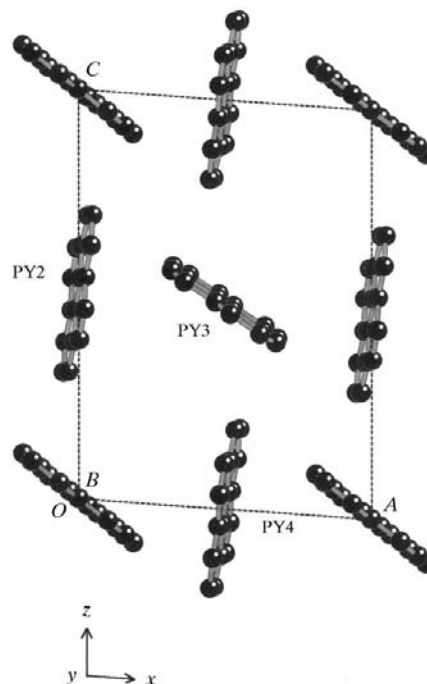

Figure 2
Section of the structure between $y = \pm 1/4$, showing the four pyrenes located about the independent centres of symmetry. Note that the PY1 shown is one of the pair which is centred at the origin of the cell and analogously for the other pyrenes. The similar but not identical orientations of PY1 and PY3, and of PY2 and PY4, gives rise to the pseudosymmetry noted in the text and misinterpreted by Biradha *et al.* (1999) as evidence for a polar structure.

[Ni(bipy)$_2$(ONO$_2$)$_2$] nets are the host species and the pyrenes the guest species.

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