The Structure of $[Ni(ethylenediamine)_2(NO_2)]BF_4$

By M. G. B. DREW, D. M. L. GOODGAME, M. A. HITCHMAN, and D. ROGERS
(*Chemistry Department, Imperial College, London, S.W.7*)

A RECENT two-dimensional crystallographic study[1] of $[Nien_2(NO_2)]ClO_4$ was interpreted as showing an approximately linear nitrite ligand bound weakly by one of its oxygens to two equidistant

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[1] F. J. Llewellyn and J. M. Waters, *J. Chem. Soc.*, 1962, 3845.

nickel atoms in a polymer chain. This novel form of nitrite group seemed doubtful to us. The Ni–O distances (2·58Å) were improbably long, and inconsistent with the strength of the ligand field shown by the electronic spectrum, which has bands at 20,240, 12,500, and ~10,900 (sh) cm.$^{-1}$ [These band energies are very similar to those found[2] for $Ni(NH_3)_4(NO_2)_2$, but are appreciably greater than those found for related nitrito-complexes.[3]]

We re-examined the crystallographic evidence and found it unconvincing. The nitrite group was ill-defined both in the projections and in the corresponding difference Fouriers calculated by us from the published data. In particular the [001] maps suggested to us a nonlinear nitrite in a disordered structure—a complication apparently not considered by Llewellyn and Waters.[1] A three-dimensional re-investigation seemed desirable.

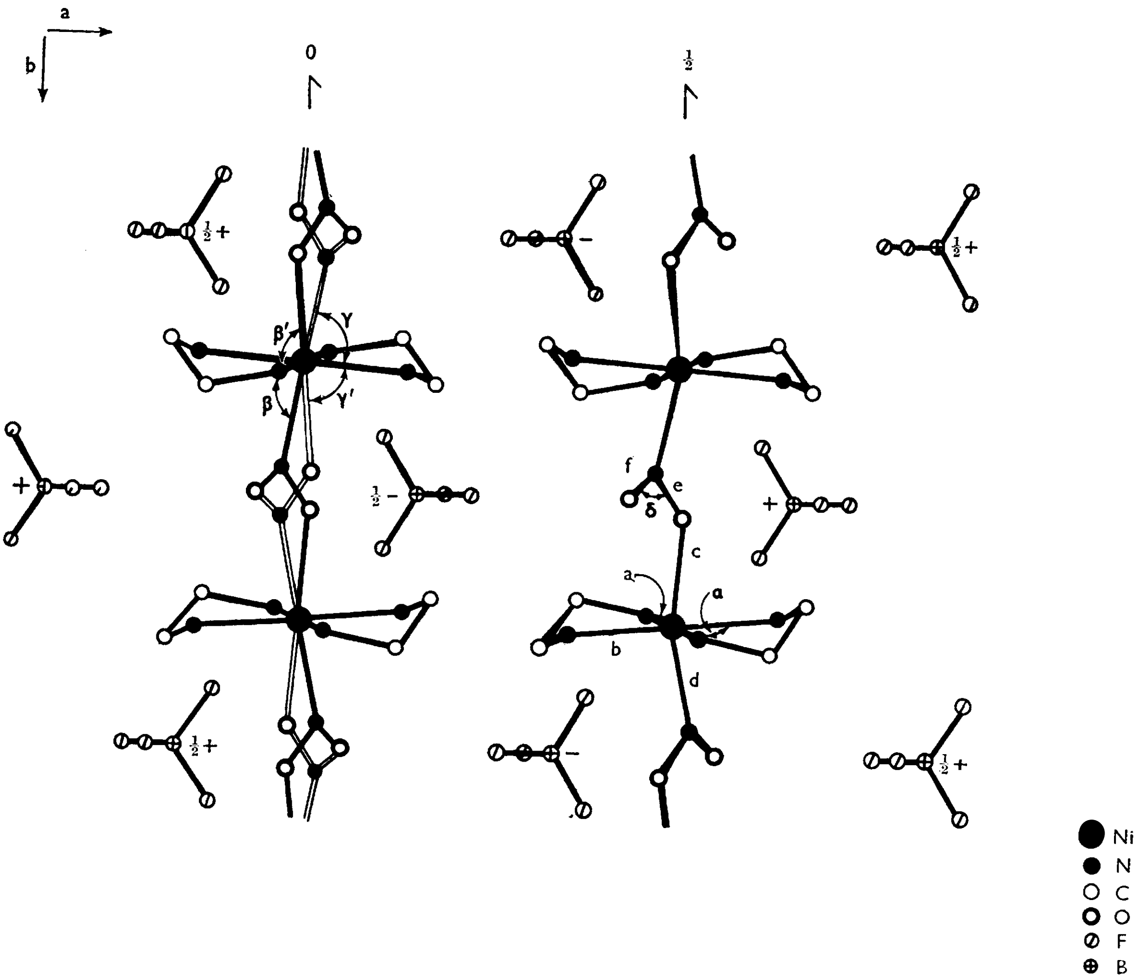

FIGURE 1. [001] *Projection of structure. Left-hand chain at* z = 0 *shows the disordered structure; the right-hand chain at* $z = \frac{1}{2}$ *is shown ordered.*

A specimen of $[Nien_2(NO_2)]BF_4$ had been prepared in this laboratory and its electronic spectrum shown to correspond exactly with that of the perchlorate. It also proved to be isomorphous,

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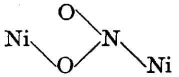
[2] C. R. Hare and C. J. Ballhausen, *J. Chem. Phys.*, 1964, **40**, 792.

[3] D. M. L. Goodgame and M. A. Hitchman, *Inorg. Chem.*, 1964, **3**, 1389.

and, as it appeared to be the more suitable of the two, it was chosen for three-dimensional study. The crystals are orthorhombic, $a = 15·142$, $b = 10·305$, $c = 8·153$Å, $Z = 4$, space group $Pn2_1a$ or $Pnma$. A structure analysis based on 811 visually estimated independent reflexions has been refined by full-matrix least squares in the centrosymmetric space group, $Pnma$, to a final value, $R = 0·138$. The structure obtained is shown in the left-hand polymer chain of Figure 1, the nickel atoms occupying centres of symmetry. All atoms, except two in the nitrite bridge, are well-defined single peaks in the three-dimensional electron-density maps, and all are related by or lie on the mirror planes of the space group $Pnma$. The two remaining atoms, however, occurred as two pairs of well-defined half-weight peaks straddling the mirror plane. All attempts to treat this as a fully ordered structure in the space group $Pn2_1a$ (whether by least-squares or difference Fouriers) have refused to refine further. We are forced to the conclusion that the space group is truly $Pn2_1a$, and that the nitrite groups are disordered. In either space group the nickel atoms lie on or near 2_1 screws, and this limits the possible ways of interpreting the disorder to one, namely that shown in the right-hand polymer chain of Figure 1. In this, one oxygen and the nitrogen of each nitrite group participate in the polymer chain: the free oxygen is equidistant (3·107Å) from two nickel atoms. Each nickel in this chain is bound to an oxygen on its lower side, and to a nitrogen on its upper side, but these two bonds are not collinear—in fact the nickel environment is no longer centrosymmetric in this space group. The bond lengths and angles compare well with those found in two related structures.[4,5] The chelate rings are again *gauche* and have the *kk′* conformation,[6] but they are less puckered than usual. The  group is nearly planar (maximum distance of an atom from the plane is 0·047Å). The angle N–Ni–O is 155·8°, and compares[5] with a similar non-linear distortion, O–Ni–O of 158·8°, but in the present structure the oxygen atom is more displaced from the axial position than is the nitrogen atom. The nitrite groups in any one chain are probably ordered (at least for considerable distances along the chain), but the disorder probably arises from random reversal of NO_2 groups in either adjacent chains or adjacent domains of chains.

The fluoborate ion is still rather poorly defined, probably due to orientational disorder. This is a feature of perchlorates[7] and has also been reported of one fluoborate.[8]

Bond lengths (Å), *Angles* (°)

(*Standard deviations from full-matrix least-squares refinement*)

a	2·117 ± 0·011	α	84·14 ± 0·46
b	2·097 ± 0·012	β	94·08 ± 0·67
c	2·215 ± 0·017	β′	100·68 ± 0·57
d	2·155 ± 0·019	γ	83·39 ± 0·69
e	1·276 ± 0·026	γ′	81·11 ± 0·59
f	1·224 ± 0·025	δ	110·78 ± 1·71

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[4] M. G. B. Drew, D. M. L. Goodgame, M. A. Hitchman, and D. Rogers, *Proc. Chem. Soc.*, 1964, 363.

[5] M. G. B. Drew and D. Rogers, preceding paper.

[6] E. J. Corey and J. C. Bailar, *J. Amer. Chem. Soc.*, 1959, **81**, 2620.

[7] P. Pauling, G. B. Robertson, and G. A. Rodley, *Nature*, 1965, **207**, 73; J. Lewis, R. S. Nyholm, and G. A. Rodley, *ibid.*, p. 72; P. Pauling, personal communication.

[8] I. C. Zimmermann, M. Barlow, and J. D. McCullough, *Acta Cryst.*, 1963, **16**, 883.