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The Diffuse X-ray Scattering and the Structure of the Iodine Chains in Bis-(1,2-benzoquinonedioximato)$_2$nickel.0·5I [Ni(BCD)$_2$.0·5I]

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Diffuse X-ray scattering from the title compound, containing linear iodine chains, indicates the formation of I_3 ions. These anions are disordered from their averaged positions. The oxidation number of the Ni atoms in this mixed-valence one-dimensional solid is 2·17.

Introduction

The electronic and structural properties of one-dimensional systems have become a field of rapidly growing interest (Yagubskii & Khidekel, 1972; Keller, 1975; Zeller, 1973). Among the systems investigated, complexes containing linear chains of metal atoms with non-integral oxidation states [*e.g.* $K_2[Pt(CN)_4]Br_{0.3}.3H_2O$, KCP, (Krogmann, 1969)] played a prominent role.

Some years ago it was proposed from incomplete X-ray data (Foust & Soderberg, 1967) and from spectroscopic evidence (Keller & Seibold, 1971) that the oxidation product of Ni(dpg)$_2$ [dpg = diphenylglyoximate $(C_6H_5)_2C_2N_2O_2H^-$] with iodine, Ni(dpg)$_2$I, contains linear iodine chains parallel to the columnar stacks of metal complex units. In this case the electron delocalization in the metal chain should be enhanced if an oxidation of the metal ions has taken place. Therefore the recent structure determination of Ni(dpg)$_2$I (Gleizes, Marks & Ibers, 1975) was of great importance, giving crystallographic proof for the reality of the proposed iodine chains.

Simultaneously some complexes with other 1,2-dionedioximato ligands and linear iodine chains have been prepared and characterized by X-ray structure determination: M(BCD)$_2$.0·5I, (M=Ni, Pd) (Endres, Keller, Moroni & Weiss, 1975) and bis(glyoximato)palladium iodide (Endres, Keller, Lehmann & Weiss, 1976).

All the above structure determinations showed evidence of disorder connected with the iodine chains. But neither could the nature of this disorder be evaluated nor the question of the oxidation state of the metal ions be answered.

In this paper we present a model for the disorder of the iodine chains and suggest an oxidation number for the central metals ions in the compound Ni(BCD)$_2$.0·5I based on the diffuse X-ray scattering.

The diffuse X-ray scattering

On rotation photographs from Ni(BCD)$_2$.0·5I (rotation axis *c*) in addition to the normal Bragg layer lines diffuse layer lines can be discerned (Fig. 1). These diffuse layer lines run perpendicular to **c*** with an interlayer spacing of $\frac{2}{3}c^*$, so that the third diffuse line coincides with the second zone of Bragg reflexions. Neglecting superstructure reflexions, the intensity along one diffuse line is monotonic, but it does not change monotonically from line to line. From a series of 'monochromatic Laue photographs' it becomes evident that the diffuse lines result from intersections of diffuse reciprocal planes with the sphere of reflexion, demonstrating the existence of a particular one-dimensional local order. A similar feature can be found in KCP (Renker & Comès, 1975).

Experimental

The rotation photograph was taken with monochromatic Mo *Kα* radiation (graphite monochromator).

In order to obtain the intensities of as many diffuse lines as possible, monochromatic Laue photographs (Mo *Kα*, LiF-monochromator) were taken with the fixed crystal having **c** at an angle of 45° to the incident beam. A cylindrical film was used with its axis perpendicular to the incident beam and **c** of the crystal. The dimensions of the crystals were about 0·2 × 0·2 × 5 mm. Fig. 2 shows a photograph obtained with this arrangement. The intensities of the diffuse lines of three films with different exposure times were measured with a microdensitometer. The scans run perpendicular to the diffuse lines, starting near the incidence point of the primary beam. In order to avoid errors by accidentally measuring reflexions on the diffuse streaks, several parallel scans with a distance of 0·3 mm were recorded on the same sheet of paper. Fig. 3 shows a set of curves obtained in this way. The constant intensities of the diffuse lines can easily be separated from the variable intensities of intersecting Bragg reflexions.

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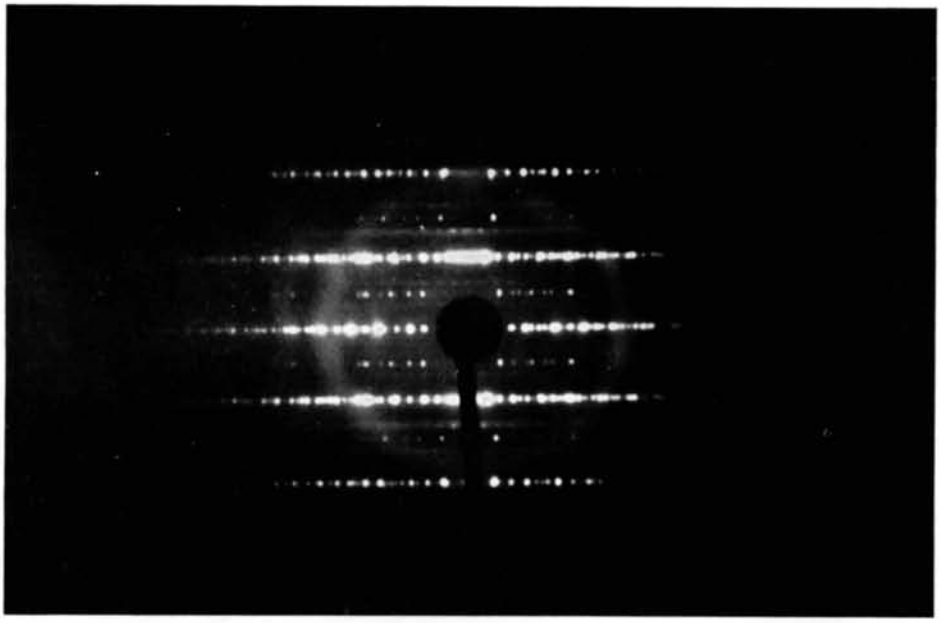

Fig. 1. Rotating crystal photograph.

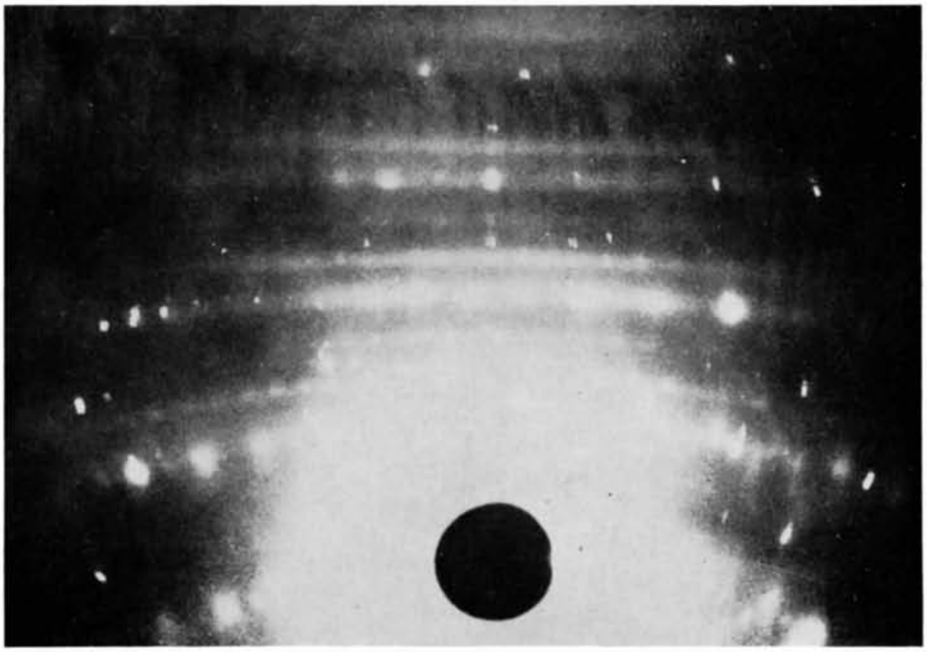

Fig. 2. Monocromatic Laue photograph.

The areas of the peaks were determined by balancing; intensities of the different films were scaled and corresponding intensities averaged. Five of the 16 diffuse lines visible on the film were too weak to be measured; their intensities were estimated visually. Polarization and rough linear absorption corrections were applied.

Interpretation of the diffuse scattering

From the diffuse scattering we may conclude that we are dealing with a one-dimensional superstructure along **c** with a repeat distance of $\frac{3}{2}c=9\cdot46$ Å. The indexing of the diffuse lines is based on this superstructure period.

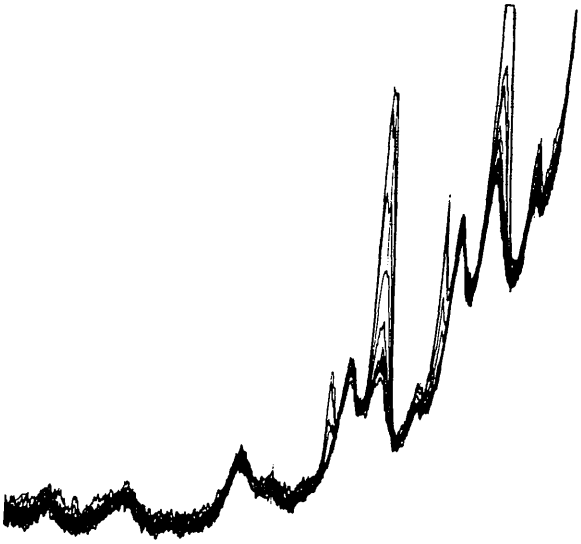

Fig. 3. Microdensitometer scans of the photograph of Fig. 2.

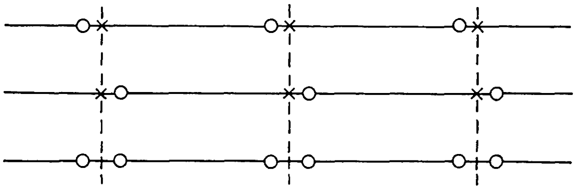

Fig. 4. Example of a one-dimensional superstructure caused by disorder. Upper two lines: × averaged sites from structure determination, ○ local sites on one chain. Lower line: overall structure by superposition of the different chains.

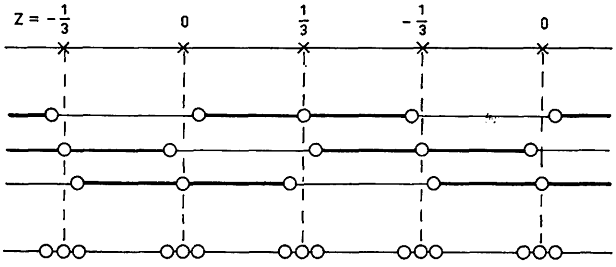

Fig. 5. Model with symmetrical I_3 groups. First line: averaged sites. Lines 2 to 4: local arrangements forming I_3 groups. Lower line: overall structure.

The structure factor for the diffuse scattering (F_d) is given by

$$F_d=F_{oa}-F_l$$

where F_{oa} is the structure factor of the 'overall structure' and F_l the structure factor of the 'local structure'. The overall structure is obtained by superimposing all the local atomic arrangements onto one single chain of atomic sites; it must not be confused with the 'averaged' structure obtained by classic X-ray structure analysis. Fig. 4 shows an example. In calculating F_d care has to be taken for the correct weighting of F_{oa} relative to F_l. The calculating procedure is illustrated by the example of Fig. 4: Let d be the distance between the averaged and the local sites, averaged sites being x_i. Then, for a given index l

$$\begin{aligned}F_{oa,\,l}&=\tfrac{1}{2}\sum_i\{\exp\left[-2\pi il(x_i+d)\right]\\&\quad+\exp\left[-2\pi il(x_i-d)\right]\}\\F_{l,\,l}&=\sum_i\exp\left[-2\pi il(x_i+d)\right]\\F_{d,\,l}&=F_{oa,\,l}-F_{l,\,l}\,.\end{aligned}$$

(The number of overall sites is twice the number of local sites.)

We started with the hypothesis that the cause of the diffuse scattering has to be sought in the iodine chain, because forming I_3^- groups in the iodine chains results in a superstructure of the observed repeat distance. We first tried a model with symmetric I_3^- ions. The averaged sites along 001 are $0,\ \frac{1}{3},\ \frac{2}{3}$ or, for simpler calculation: $-\frac{1}{3},0,\frac{1}{3}$. With a displacement parameter d, and all possible sites obtained by the formation of I_3^- ions as shown in Fig. 5, we obtain

$$\begin{aligned}F_{oa,\,l}&=\tfrac{1}{3}\{1+\exp\left(-2\pi il/3\right)+\exp\left(2\pi il/3\right)\\&\quad+\exp\left(-2\pi ild\right)+\exp\left(2\pi ild\right)\\&\quad+\exp\left[-2\pi il(\tfrac{1}{3}-d)\right]+\exp\left[2\pi il(\tfrac{1}{3}-d)\right]\\&\quad+\exp\left[-2\pi il(\tfrac{1}{3}+d)\right]+\exp\left[2\pi il(\tfrac{1}{3}+d)\right]\}\\F_{l,\,l}&=1+\exp\left[-2\pi il(\tfrac{1}{3}-d)\right]+\exp\left[2\pi il(\tfrac{1}{3}-d)\right]\\F_{d,\,l}&=F_{oa,\,l}-F_{l,\,l}\,.\end{aligned}$$

With this model, it is possible to arrive at a displacement parameter d which explains the intensities of the superstructure diffuse lines with $l\neq 3n$ quite well, but the intensities of the fundamental diffuse lines with $l=3n$ are calculated as zero, in disagreement with experimental observation.

If structure factors of models with unsymmetrical I_3 groups are calculated, non-zero intensities are obtained for $l=3n$. But it proved impossible to find a set of displacement parameters in reasonable agreement with the observed intensities. Therefore we went on working with symmetrical I_3 groups and searched for an additional disorder which accounted for the intensities with $l=3n$.

One possibility was to think of a displacement in the metal chain, too, such that the metal–metal distance of one half of *c* is maintained and the whole metal chain is displaced along **c**. Such a model was able to account quite well for the observed intensities ($R=0·164$), but seemed improbable because the U_{33} component of the temperature factor of I is significantly greater than the other U_{ij} values, but no effect like this can be observed with the Ni atoms (Endres, Keller, Moroni & Weiss, 1975).

If an additional disorder in the iodine chains, which is to be explained as a shift of the whole I_3 units out of their averaged positions, is taken into account, then non-zero structure factors are calculated for $l=3n$. Thus we are dealing with two displacement parameters, the first one leads to the I_3 groups, the second displaces the groups as a whole. This model is calculated as follows (Fig. 6): Writing d_1 for $\exp(-2\pi ild)$, $-d_1$ for $\exp(2\pi ild)$, (d_1+d_2) for $\exp[-2\pi ild(d_1+d_2)]$ and so on, we obtain

$$\begin{aligned}F_{oa,1}=\tfrac{1}{6}\{&d_2+(-d_2)+(d_1-d_2)+(-d_1+d_2)+(d_1+d_2)\\&+(-d_1-d_2)+(\tfrac{1}{3}+d_2)+(-\tfrac{1}{3}-d_2)+(-\tfrac{1}{3}+d_2)\\&+(+\tfrac{1}{3}-d_2)+(\tfrac{1}{3}+d_1+d_2)+(-\tfrac{1}{3}-d_1-d_2)\\&+(\tfrac{1}{3}+d_1-d_2)+(-\tfrac{1}{3}-d_1+d_2)+(\tfrac{1}{3}-d_1+d_2)\\&+(-\tfrac{1}{3}+d_1-d_2)+(\tfrac{1}{3}-d_1-d_2)+(-\tfrac{1}{3}+d_1+d_2)\}\end{aligned}$$

$$F_{1,1}=d_2+(\tfrac{1}{3}-d_1+d_2)+(-\tfrac{1}{3}+d_1+d_2)$$

$$F_{d,1}=F_{oa,1}+F_{1,1}\,.$$

The best *R* obtained is 0·164 ($B=0·73$) for $d_1=0·0374$ and $d_2=0·0260$; observed and calculated structure factors are listed in Table 1.

Table 1. *Observed and calculated structure factors*

l	F_{obs}	F_{calc}
1	13·08	11·59
2	18·08	18·56
3	63·50	61·18
4	52·50	39·16
5	16·68	26·58
6	46·58	52·53
7	50·18	48·70
8	12·08	18·81
9	21·50	18·57
10	41·38	45·51
11	2·00	6·80
12	7·69	1·00
13	35·88	35·90
14	1·28	3·79
15	2·00	1·97
16	29·18	23·96

Results and discussion

By investigating the diffuse X-ray scattering of $Ni(BCD)_2.0·5I$ we found disordered groups of three atoms along chains in the [001] direction. Because of the abnormally high U_{33} component of the temperature factor for I we identify those groups of three atoms with I_3^- ions. Thus we are actually not dealing with equidistant chains of I atoms, but the I positions are ordered along one chain in such a way as to form symmetrical I_3^- ions. The distances within one I_3^- entity are 2·80 Å, two adjacent anions being 3·86 Å apart. The I_3^- groups are shifted along the chain by 0·25 Å from their averaged positions in such a way as to maintain the one-dimensional order (Fig. 7). (Here we interpret our findings in terms of a static disorder, though a dynamical effect cannot be ruled out.) As a precession photograph of the 0*kl* plane shows that the superstructure reflexions on the diffuse layer lines have the same spacing as the fundamental reflexions, some degree of ordering between adjacent iodine chains can be assumed.

The compound $Ni(BCD)_2.0·5I$ may serve as another model for the blue iodine–starch adduct. Some other compounds where iodine chains are included in an organic matrix have been discussed: Huml (1967) reports a projection of the structure of the iodide of the *N,N'*-diphenyl-*p*-phenylenediamine radical, a compound that exhibits diffuse X-ray scattering too. Reddy, Knox & Robin (1964) communicate the structure of the triiodide of benzamide, $HI_3.2C_6H_5CONH_2$, where slightly bent asymmetric I_3^- units form zigzag chains with intermolecular I–I distances between 2·90

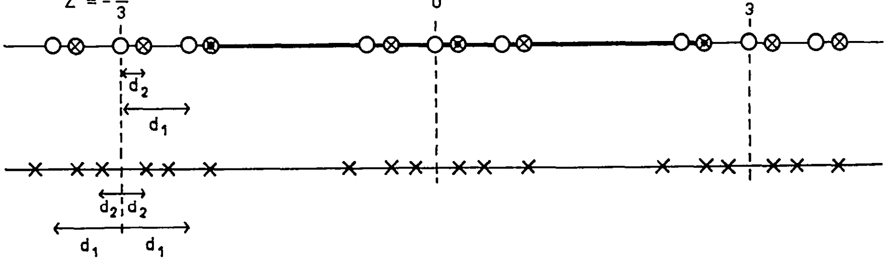

Fig. 6. Model with displaced symmetrical I_3 groups. Upper line: ○ averaged position after forming I_3 groups (displacement d_1), corresponding to lower line of Fig. 5. ⊗ new positions after shift d_2 in one direction. ⊙ local atomic sites of one I_3 unit. Lower line: new overall positions.

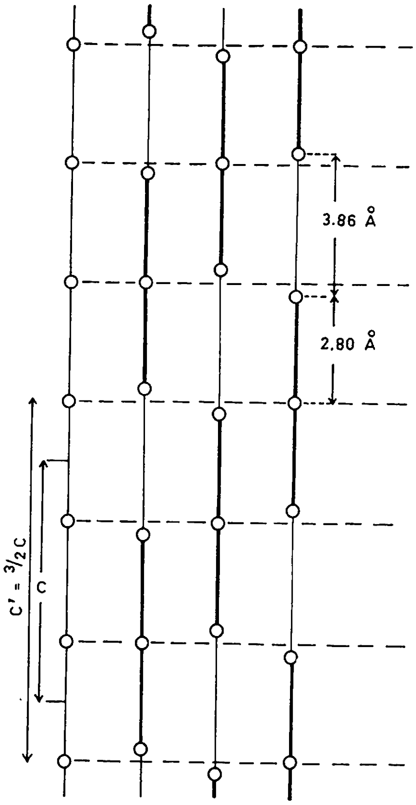

Fig. 7. The different possibilities of forming I groups, not showing the additional displacement d_2 of the whole I_3 groups. Left row: averaged sites. Right rows: The possible arrangements of I_3 units, resulting in the overall structure shown in the lower line of Fig. 5.

and 2·96 Å and intramolecular distances of 3·80 Å. Saenger & Noltemeyer (1975) report on an α-cyclodextrin–polyiodide adduct with chains of alternating I_3^- and I_2 groups. Some I–I distances in compounds containing isolated I_3^- anions are given by Mooney Slater (1959).

Probably a disorder similar to that described here explains the unusual behaviour of the temperature factor of the I atom in Ni(dpg)$_2$I (Gleizes, Marks & Ibers, 1975). The same is true for bis(glyoximato)palladium iodide, where diffuse X-ray scattering is detectable, too. Therefore we may conclude that in none of the bis-(1,2-dionedioximato)metal.I_x complexes described so far are the iodine chains equidistant, but that I_n entities are formed, where $n=3$ for Ni(BCD)$_2$.0·5I.

This feature gives an important hint to the oxidation state of the metal atoms in the bis-(1,2-dionedioximato)metal.I_x compounds. Mehne & Wayland (1975) prefer, from a discussion of the solution ESR spectra, a formulation with trivalent Ni atoms in Ni(dpg)$_2$I, though they discuss the possibility of $Ni^{2.33+}$, too.

As it is reasonable to identify the I_3 units as anions, the oxidation state of the Ni atoms in Ni(BCD)$_2$.0·5I is 2·17. If the I atoms in Ni(dpg)$_2$I and bis(glyoximato)palladium iodide behave in the same way, the oxidation state of the metal atoms is 2·33, approaching the 'magic oxidation number' of the Krogmann-type compounds, such as KCP.

Note added in proof: Recent Raman and Mössbauer experiments on the compound described in this paper confirm the existence of I_3^- anions in the Ni(BCD)$_2$.0·5I lattice [T. J. Marks, D. F. Webster, S. L. Ruby & S. Schultz (1976), private communication, submitted to *Chem. Commun.*]

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