The OD Structure of Di-μ-chloro-tetranitrosyldicobalt,

[Co(NO)$_2$Cl]$_2$

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The crystal structure of di-μ-chloro-tetranitrosyldicobalt is characterised in terms of the family of structures represented by the OD groupoid symbol:

$$P \; b \; a \; (m)$$
$$\{n_{1,2} \; n_{2,\bar{1}} \; (a_{\frac{1}{2}})\}$$

The relationship between the different crystalline modifications of [Co(NO)$_2$Cl]$_2$, hitherto reported, is demonstrated.

A part from an orthorhombic modification, the crystal structure of which has been determined,[1] several different crystalline forms of di-μ-chloro-tetranitrosyldicobalt have been reported.[1,2] The purpose of this paper is to illustrate the relationship between these different modifications by showing that they are all members of the same OD family of structures. The nomenclature used is in accordance with the textbook *Lehrgang über OD-Strukturen* by K. Dornberger-Schiff.[3]

The approximate cell dimensions and the space groups of the different crystalline modifications of [Co(NO)$_2$Cl]$_2$ reported to date are given in Table 1. In the collection of the intensity data for modification I of this table, whose crystal structure was found[1] to consist of alternate ordered ($z = 0$) and dis-

Table 1. Approximate unit cell dimensions and space groups for some crystalline modifications of [Co(NO)$_2$Cl]$_2$.

	Unit cell dimensions	Space group [4]	Ref.
I	$a = 12.87$ Å, $b = 6.18$ Å, $c = 11.25$ Å	No. 55, *Pbam*	1
II	$a = 12.81$ Å, $b = 11.11$ Å, $c = 6.14$ Å	No. 62, *Pnma*	2
III	$a = 6.36$ Å, $b = 6.18$ Å, $c = 12.63$ Å, $\beta = 120°$	No. 14, *P2$_1$/c*	1, 2
IV	$a = 11.25$ Å, $b = 6.42$ Å, $c = 6.18$ Å	No. 63, *Cmcm*	1

ordered $(z = \frac{1}{2})$ layers perpendicular to the c-axis, the following systematic reflection conditions were noted:

1) $0kl$: $k = 2n$
2) $h0l$: $h = 2n$
3) $h0l$: $l = 2n$, $h = 4n$
4) $h0l$: $l = 2n + 1$, $h = 4n + 2$

The existence of extra reflection conditions, such as 3) and 4), which are not required by space group symmetry, is typical of OD structures.[3] Such structures can often be recognised by the presence of diffuse streaks on Weissenberg or rotation photographs. No such phenomena were observed during the investigation of the $[Co(NO)_2Cl]_2$ system. A large number of different crystalline modifications in addition to those whose unit cell dimensions and space groups were definitely characterised (*cf.* Table 1) were, however, observed. Whereas all crystals were found to have two axes of approximately 6.18 Å and 12.87 Å (modification IV of Table 1 in reality showing a few very weak reflections which would require a doubling of the b-axis), the third axis was often a multiple of 11.25 Å. Festoons of discrete, very closely placed reflections could thus sometimes be seen on Weissenberg photographs taken about the 6.18 Å axis. This seemed to indicate [3] that the crystals were built up of ordered layers, the stacking of which was disordered, the cell dimensions within the layers being approximately 6.18 Å and 12.87 Å, and the dimension perpendicular to the layers a multiple of 11.25 Å.

According to reflection conditions 1) and 2), respectively, for every atom in (x, y, z) there must exist an identical atom in $(x', 1/2 + y, z)$, and one in $(1/2 + x, y', z)$. Since these three atoms all have the same z value, they must lie in the same plane and thus belong to the same layer, L_0. The minimum symmetry of this layer is $Pba(2)$, although $Pba(m)$ is also consistent with the reflection conditions. If it is assumed that L_0 has the symmetry $Pba(m)$ with the b glide plane in $x = 1/4$, the a glide plane in $y = 1/4$, and the mirror plane in $z = 0$, the equipoints of L_0 are:

(x, y, z); $(1/2 - x, 1/2 + y, z)$; $(1/2 + x, 1/2 - y, z)$; $(\bar{x}, \bar{y}, z)$
$(x, y, \bar{z})$; $(1/2 - x, 1/2 + y, \bar{z})$; $(1/2 + x, 1/2 - y, \bar{z})$; $(\bar{x}, \bar{y}, \bar{z})$.

Reflection conditions 3) and 4) require that for every atom with the coordinates (x, y, z) in L_0 there must exist an identical atom in the next layer, L_1, with the coordinates $(x \pm 1/4, y'', z + 1)$, where the symbol $\pm$, contrary to normal usage, here denotes $+$ or $-$, the unit vector between two consecutive layers, in the non-periodic direction perpendicular to the layers, being defined [3] as $\vec{c_0}$. An atom in (x, y, z) is thus related to these two possible positions by a partial symmetry operation which can be represented as $_{0,1}[1\ n_{2,\frac{1}{4}}\,(1)]$ or $_{0,1}[1\ n_{2,\bar{\frac{1}{4}}}$ $(1)]$ for $(x + 1/4, y'', z + 1)$ and $(x - 1/4, y'', z + 1)$, respectively. If, for convenience, the glide plane is placed in $y = 1/4$, the coordinates of the atom generated from that in (x, y, z) by one of these partial operations are then $(x \pm 1/4, 1/2 - y, z + 1)$. Since the layers L_0 and L_1 are identical, L_1 must also have the symmetry $Pba(m)$, and if the so-called λ-symmetry operations within the layer are applied to the atom in $(x \pm 1/4, 1/2 - y, z + 1)$, the following equivalent positions are obtained for L_1:

$(x \pm 1/4,\ 1/2 - y,\ z + 1);\ (1/2 - x \mp 1/4,\ \bar{y},\ z + 1);$
$(1/2 + x \pm 1/4,\ y,\ z + 1);\ (\bar{x} \mp 1/4,\ 1/2 + y,\ z + 1);$
$(x \pm 1/4,\ 1/2 - y,\ \bar{z} + 1);\ (1/2 - x \mp 1/4,\ \bar{y},\ \bar{z} + 1);$
$(1/2 + x \pm 1/4,\ y,\ \bar{z} + 1);\ (\bar{x} \mp 1/4,\ 1/2 + y,\ \bar{z} + 1).$

It is thus seen that there are also other partial symmetry operations which relate $(x,\ y,\ z)$ to the equipoints of L_1. For example, $(x,\ y,\ z)$ is related to $(\bar{x} \mp 1/4,\ 1/2 + y,\ z + 1)$ by the partial symmetry operation $_{0,1}[n_{1,2}\ 1\ (1)]$, the glide plane being situated in $x = 1/8$ for $(\bar{x} + 1/4,\ 1/2 + y,\ z + 1)$ and in $x = -1/8$ for $(\bar{x} - 1/4,\ 1/2 + y,\ z + 1)$. Similarly, the partial symmetry operations $_{0,1}[1\ 1\ (a_{\frac{1}{4}})]$ and $_{0,1}[1\ 1\ (a_{\bar{\frac{1}{4}}})]$ convert $(x,\ y,\ z)$ into $(1/2 + x - 1/4,\ y,\ \bar{z} + 1)$ and $(1/2 + x + 1/4,\ y,\ \bar{z} + 1)$, respectively.

The total symmetry of a pair of consecutive layers, L_p and L_{p+1}, can thus be expressed in terms of the OD groupoid

$$P\ b\ a\ (m)$$
$$\{n_{1,2}\ n_{2,\bar{1}}\ (a_{\frac{1}{4}})\}$$

which can be illustrated schematically as, *e.g.*, in Fig. 1a. The repeat distance in the non-periodic direction, corresponding to the unit vector, $\vec{c_0}$, is 5.63 Å, *i.e.* one-half the length of the c-axis of modification I (*cf.* Table 1).

It is apparent from Fig. 1a that, whereas L_0 is converted into L_1 by the partial symmetry operations $_{0,1}[n_{1,2}\ n_{2,\bar{1}}\ (a_{\frac{1}{4}})]$, L_1 is converted into L_2 by the operations $_{1,2}[n_{1,2}\ n_{2,\frac{1}{4}}\ (a_{\bar{\frac{1}{4}}})]$. In other words, successive layers are related to one another by the translation $\alpha \vec{a}/4$ where α can take the value $+1$ or -1. If α is alternately $= \pm 1$, the arrangement depicted in Fig. 1a is obtained. This corresponds to an ordered orthorhombic structure ("maximum degree of order", MDO$_1$) with the unit cell dimensions $a = 12.87$ Å, $b = 6.18$ Å, $c = 2c_0 = 11.25$ Å, and space group *Pnam*, which is seen, by the relevant axial transformation, to be identical with the orthorhombic modification reported by Bertinotti *et al.*[2] (*cf.* II, Table 1).

An oblique stacking of the layers, *i.e.* $\alpha = +1$ only, as illustrated in Fig. 1b, results in an ordered monoclinic structure (MDO$_2$) with space group [4] No. 14, $P2_1/c$, $\vec{a}_{\mathrm{mon}} = 1/4\ \vec{a} + \vec{c_0}$, $\vec{b}_{\mathrm{mon}} = \vec{b}$, $\vec{c}_{\mathrm{mon}} = \vec{a}$, and $\beta \approx 120°$. The unit cell thus agrees well with that reported for modification III (*cf.* Table 1).

The layer sequence corresponding to the partially disordered modification I, illustrated in Fig. 1c, is obtained from translations with the following α-values: $\alpha_1 = \alpha_4 = +1$; $\alpha_2 = \alpha_3 = -1$. The ordered structure (MDO$_3$) would have $c = 4c_0 = 22.50$ Å, whereas the structure investigated,[1] which had $c = 2c_0 = 11.25$ Å is obtained by superimposing the layers L_2, L_3 and L_4 on L_0, L_1 and L_2. The superposition of layers L_1 and L_3 is seen to result in the disordered arrangement observed in $z = 1/2$. As mentioned in the previous paper,[1] the disorder in $z = 1/2$ can also be reproduced in terms of Ito twinning. This description is, of course, completely equivalent to the order-disorder description, but the latter has the advantage that it more clearly shows the relationship between *all* the members of the family of structures.

Modification IV (*cf.* Table 1) corresponds to a fictitious structure known as the "superposition structure". This structure is the same for all members of the OD family and is obtained by shifting any given arrangement through
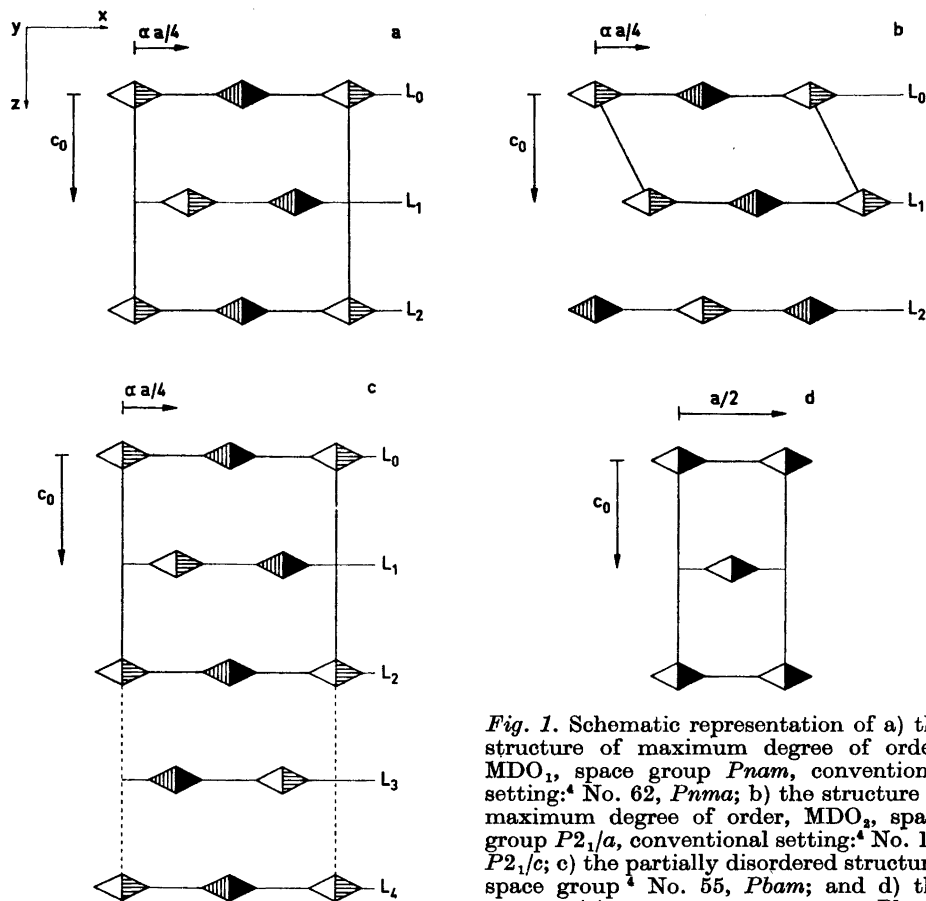
Fig. 1. Schematic representation of a) the structure of maximum degree of order, MDO$_1$, space group *Pnam*, conventional setting:[4] No. 62, *Pnma*; b) the structure of maximum degree of order, MDO$_2$, space group *P2$_1$/a*, conventional setting:[4] No. 14, *P2$_1$/c*; c) the partially disordered structure, space group [4] No. 55, *Pbam*; and d) the superposition structure, space group *Bbmm*, conventional setting:[4] No. 63, *Cmcm*. $\vec{c_0}$ denotes the unit vector in the non-periodic direction perpendicular to the layers, L_p, while α is a constant which can take the value $+1$ or -1. *Notation* a) b) and c): Horizontally shaded triangles, $+y$. Vertically shaded triangles, $1/2+y$. Empty triangles, $-y$. Filled triangles, $1/2-y$. d): Empty triangles, $-y$ and $1/2+y$. Filled triangles $+y$ and $1/2-y$.

$\vec{a}/2$ and then superimposing it on the original arrangement (*cf.* Fig. 1d), *i.e.* $\hat{\varrho}(x, y, z) = \frac{1}{2}[\varrho(x, y, z) + \varrho(x+1/2, y, z)]$ where $\hat{\varrho}(x, y, z)$ represents the superposition structure and $\varrho(x, y, z)$ the real structure.

It is thus seen that the most satisfactory description of the crystal structure of [Co(NO)$_2$Cl]$_2$ is obtained in terms of the family of structures represented by the OD groupoid symbol

$$P\,b\,a\ (m)$$
$$\{n_{1,2}\ n_{2,\bar{1}}\ (a_{\bar{1}})\}$$

This means that, since the structures of all modifications can be derived from the ordered layer $(z=0)$ of modification I (*cf.* Fig. 2a, Ref. 1), the $[Co(NO)_2Cl]_2$ molecule must be dimeric and the alternative open-chain configuration [1] can therefore be rejected. A similar dimeric structure has recently been found [5] for $[Fe(NO)_2I]_2$, whereas $[Co(NO)_2I]_n$, and probably even $[Co(NO)_2Br]_n$, have chain structures.[2,5]

In the above discussion it has throughout been assumed that the cobalt and chlorine atoms lie in a mirror plane. In the determination of the crystal structure of modification I, it was not, owing to the paucity of the data, however, possible to decide unequivocally between *Pbam* and its acentric counterpart *Pba2*, the structure being eventually described in terms of *Pbam*. The corresponding acentric space groups for the different modifications can, however, be derived, in an analogous manner, if the family is instead assumed to be characterised by the OD groupoid.

$$P\,b\,a\ (2)$$
$$\{n_{1,2}\ n_{2,\bar{1}}\ (2_2)\}$$

REFERENCES

1. Jagner, S. and Vannerberg, N.-G. *Acta Chem. Scand.* **21** (1967) 1183.
2. Bertinotti, F., Corradini, P., Diana, G., Ganis, P. and Pedone, C. *Ric. Sci. Rend.* **A 3** (1963) 210.
3. Dornberger-Schiff, K. *Lehrgang über OD-Strukturen*, Akademie-Verlag, Berlin 1966.
4. *International Tables for X-ray Crystallography*, Kynoch Press, Birmingham 1959.
5. Dahl, L., de Gil, E. and Feltham, R. *J. Am. Chem. Soc.* **91** (1969) 1653.