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## *Ab Initio* Structure Determination From Powder Data Using Direct Methods

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### Abstract

An *ab initio* structure determination was carried out on the basis of powder data using the programs developed by Jansen, Peschar & Schenk [*J. Appl. Cryst.* (1992a), **25**, 231–236; *J. Appl. Cryst.* (1992b), **25**, 237–243; *Z. Krist.* (1993), **206**, 33–43]. The results give a very good approximation to the single crystal structure. The main problems in structure determination from powder data so far are the determination of the correct space group and a better possibility than Rietveld refinement to refine the structural model coming out of the direct methods.

### 1. Introduction

In cooperation with the Department of Chemistry at the University of Ioannina and the Institute of Geology and Mineral Exploration in Athens, a structure determination was carried out on a series of

metallochloranilate compounds. These compounds show a very high grade of twinning, as well as absorption effects. In general, it is impossible to select non-twinned single crystals large enough for data collection on a four-circle diffractometer.

As a first example for *ab initio* structure determination from powder data, the compound disodium bis[3,6-dichloro-4,5-dihydroxy-3,5-cyclohexadiene-1,2-dionato(2-)] dioxouranium hexahydrate (Bram *et al.*, 1994) was selected. The pattern of the sample is rather complex, as well as the structure, which contains 22 atoms in the asymmetric unit.

Structure determination by powder data was attempted using two methods, Patterson (Brüderl *et al.*, 1994) and direct methods. To fit the powder pattern and separate overlapping intensities, the programs developed by Jansen, Peschar & Schenk (1992a,b, 1993) were used for optimal symbolic addition. In the subsequent calculations, the *Xtal3.0* system (Hall & Stewart, 1990) was used.

## 2. Experimental

The data set was collected on a computer-controlled step-scanned Guinier diffractometer, with a scintillation detector in asymmetric transmission geometry, a copper X-ray tube and a Johansson monochromator [germanium (111),  $2\theta_{\text{mon}} = 27.279^\circ$ ] and  $6 \leq 2\theta \leq 92^\circ$ .

The step width was chosen to be  $0.01^\circ$  ( $2\theta$ ), which is  $\frac{1}{10}$  of the usual halfwidth of our samples. The measuring time per step was set to 3 s; the data collection was repeated 20 times for the complete pattern, which results in a total measuring time of 60 s per data point. For the calculation of the intensities, the correction formula for the plane way of X-rays was taken as

$$\text{LPG}(\theta) = \frac{1 + \cos^2(2\theta) \cos^2(2\theta_{\text{mon}})}{4 \sin(\theta) \cos^2(\theta)}. \quad (1)$$

The sample rotated with a frequency of 5 Hz and the particle size was at a maximum of  $30 \mu\text{m}$ , as determined by microscope.

## 3. Structure determination

In view of the peak overlap to be expected in a powder diffractogram, a data set with a very high resolution is needed. The measurement of the sample resulted in a rather complex pattern (see Fig. 1), caused by the relatively large unit cell [monoclinic,  $a = 12.217$  (2),  $b = 16.543$  (3),  $c = 5.9206$  (1) Å,  $\beta = 102.57$  (1)°]. The pattern showed significant overlap; among the 527 present reflections, 317 overlapped within half of the halfwidth, determined in the fitting process.

### 3.1. Indexing and space-group determination

The indexing program from Visser (1969) was used successfully for the determination of the lattice parameters and the Bravais type, resulting in the parameters above and the centring type (I). In order to determine the structure of a compound, the correct space group is needed. The routines used are only able to determine the lattice parameters and the centring type. In our case, non-overlapping reflections were observed, which contradicted possible

extinction rules. Thus, the symmorphic space groups  $I2$ ,  $Im$  and  $I2/m$  were allowed.

The data were fitted according to  $I2/m$  with *LSQPROF* (Jansen, Peschar & Schenk, 1992a) and the resulting intensities were separated in the case of overlap by equipartitioning. After correcting to  $F$  and normalization by *NORMAL* (Main, 1985), the distribution of the  $E$  values indicated non-centrosymmetry, even though the U atom had to be on a special centrosymmetric position resulting from the chemical stoichiometry, which should strengthen the indication for centrosymmetry. Thus, the space group  $I2/m$  appeared to be improbable.

In addition, a Patterson map was calculated and Harker sections  $u0w$  and  $0v0$  were considered. Unfortunately, due to the heavy atom in the centrosymmetric position, there were as many indications for  $I2$  as for  $Im$ . It was thus impossible to determine the space group from the Patterson map.

For more information, the  $\langle E^{2n} \rangle$  moments were tested for the class of the  $h0l$  reflections. The distribution showed non-centrosymmetric values for these moments. In combination with the knowledge that the uranium has a centrosymmetric arrangement, this result was taken as an indication to start the first trial of a solution with space group  $Im$ . It was not taken for granted because of the low number of  $h0l$  reflections.\*

### 3.2. Fitting and separating overlapping reflections

The background was modelled by a polynomial of the fourth degree and the pseudo-Voigt function was used to fit the peak shape. The angular dependence of the half width was modelled separately for the Lorentzian and Gaussian components by the formula given by Cagliotti, Paoletti & Ricci (1958). As stated by David & Matthewman (1985), the Gaussian and Lorentzian half-width parameters are almost independent and the half widths can therefore be added linearly, using the mixing parameter  $\eta$ .

After five least-squares cycles, the resulting intensity values were taken as single peaks if the distance between the peaks was more than half of the half width. The data obtained in this way were stored in two files, one with 210 single reflections and the other with 317 overlapping reflections.

In the next step, the overlapping intensities were decomposed into single crystal-like intensities by the procedure of Jansen, Peschar & Schenk (1992b) using the programs *ITOF*, *NORMAL*, *TRIQUA* and *DOREES*. The decomposition needed five cycles. The chosen values for the limit parameters used by

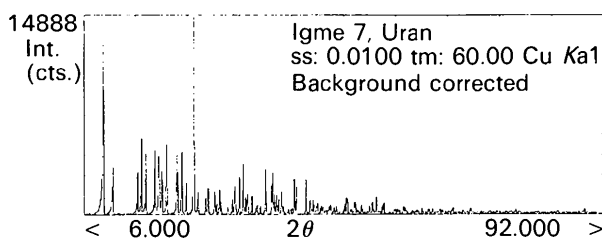


Fig. 1. Powder diffraction pattern of the sample.

\* A list of powder data has been deposited with the IUCR (Reference: SE0140). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *DOREES* values for  $M_{\text{strong}}$  and  $M_{\text{weak}}$ 

<i>DOREES</i> cycle no.	$M_{\text{strong}}$	$M_{\text{weak}}$	Single reflection no.	Overlapping reflection no.
1	10	20	217	310
2	10	20	259	268
3	20	40	304	223
4	20	40	388	139
5	20	40	470	57
—	—	—	527	—

*DOREES* (see Jansen, Peschar & Schenk, 1992b) are given in Table 1. Table 1 shows that after five cycles, all the reflections were separated successfully. A comparison with the single-crystal data showed better agreement compared with an equipartitioned data set. The separated reflection data were then used for direct methods.

### 3.3. Structure determination by direct methods

Structure solution was attempted using two direct methods packages, one the single-crystal package *Xtal3.0* (Hall & Stewart, 1990) and the other an especially developed version for powders of the *SIMPEL88* (Peschar, 1990) program. The main change in the latter is a weighting scheme which takes into account the overlap of reflections and treats the overlapping reflections in the phasing process correctly (Jansen, Peschar & Schenk, 1993).

Both direct methods programs led to the same solution.

A default run of *Xtal3.0* resulted in a map with eight positions, which seemed chemically reasonable. There were only five ghost peaks in the neighbourhood of the U atom, but peak numbers 2 and 3 in the Fourier-map were assigned to Cl atoms and with these it was possible to decide which peaks were the ghost peaks. In the subsequent least-squares refinement a damping factor of 0.25 was used. The remaining positions were found in four cycles of Fourier and least-squares analysis. The Fourier map only showed higher peaks in the neighbourhood of the U atom, which were too close to be atomic positions.

The default run of the powder version of *SIMPEL88* (Jansen, Peschar & Schenk, 1993) led to 16 chemically meaningful positions, but two further Fourier and least-squares cycles were needed to obtain the remaining positions. This result shows that the use of weights, with respect to overlap, results in a better chance of solving structures *ab initio* with powder data.

It should be mentioned that the Fourier maps contained in both cases more peaks, being positions of the single-crystal solution. However, these peaks could be recognized as atoms only in the comparison of the model and the single-crystal positions and not by distances and angles.

The final least-squares remained stable up to a damping factor of 0.75.

### 3.4. Refinement of the structural model

After the structure determination, a refinement test of the model was performed in two different ways. In the first step, the decomposed intensities/ $F$  values were refined with the usual least-squares routine programmed for single-crystal applications. The second test was to refine the structural model with a Rietveld algorithm. For the first test, the program *CRYLSQ* in the *Xtal3.0* system was used, for the second *DBW4.2* (Howard & Snyder, 1989).

Using the single-crystal refinement program, different parts of the refinement were tested. The refined parameters and the results are shown in Table 2. The resulting solutions based on the decomposed data set are compared with the single-crystal positions and the average squared distance of

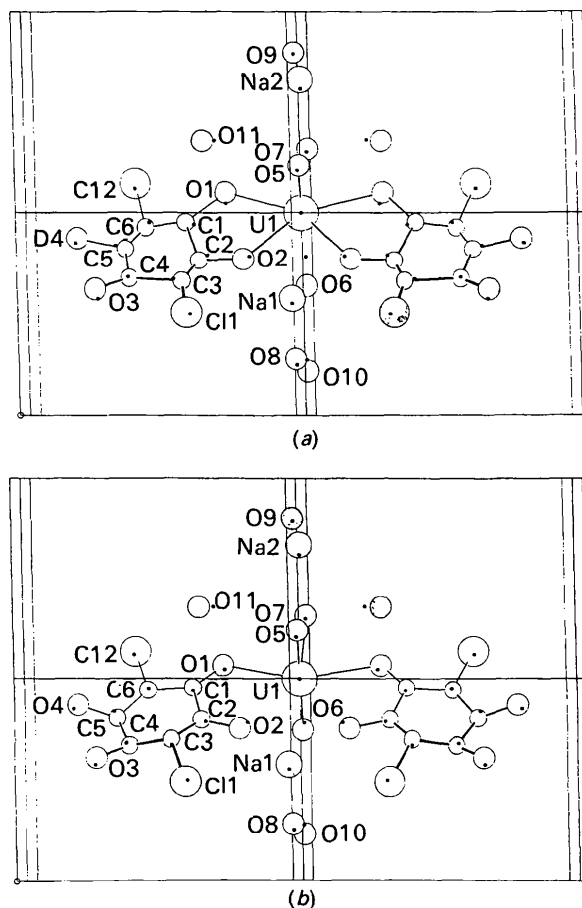


Fig. 2. (a) Comparison of powder data refinement with  $U_{ov}$ , experimental weights with the single-crystal positions (black dots) in the *ab*-projection. (b) Comparison of powder data refinement with  $U_{ov}$ , experimental weights and restraints with the single-crystal positions (black dots) in the *ab*-projection.

Table 2. Comparison of the different powder refinements

Refined parameters	Par. no.	Weights	Agreement figures						Restrains	Average squared difference to single crystal
			$R$	$R_{wp}$	GOF	$R$	GOF	all $ F $		
$Sk, x, y, z, U_{ov}$	59	Unit weight	23.9	28.0	35.2	29.4	33.5	40.2	No	0.147
$Sk, x, y, z, U_{ov}$	59	$w = 1/\sigma$	24.2	22.1	3.76	29.8	29.4	4.77	No	0.135
$Sk, x, y, z, U_{iso}$	81	$w = 1/\sigma$	23.9	21.3	3.72	29.6	28.7	4.76	No	0.159
$Sk, x, y, z, U_{ov}$	59	Unit weight	24.6	29.0	36.4	29.6	34.4	41.2	Yes	0.094
$Sk, x, y, z, U_{ov}$	59	$w = 1/\sigma$	25.1	22.7	3.86	30.5	25.1	4.83	Yes	0.072
$Sk, x, y, z, U_{iso}$	81	$w = 1/\sigma$	24.7	22.0	3.85	29.6	28.7	4.81	Yes	0.092

Table 3. Comparison of atomic positions (single crystal/powder)

Atom	$x_{sc}$	$y_{sc}$	$z_{sc}$	$\Delta$ (Å)	$x_{pow}$	$y_{pow}$	$z_{pow}$
U	1/2	1/2	1/2	0	1/2	1/2	1/2
Cl1	0.2480 (2)	0.6820 (1)	-0.1689 (3)	0.09 (3)	0.244 (4)	0.686 (3)	-0.163 (7)
Cl2	0.5599 (2)	0.8093 (1)	0.7651 (3)	0.13 (2)	0.569 (4)	0.807 (3)	0.781 (7)
Na1	0.2751 (3)	1/2	0.9199 (5)	0.17 (6)	0.288 (9)	1/2	0.913 (19)
Na2	0.8088 (3)	1/2	0.6098 (5)	0.38 (7)	0.834 (10)	1/2	0.581 (19)
O1	0.5229 (4)	0.6394 (3)	0.5852 (6)	0.22 (5)	0.533 (10)	0.644 (6)	0.619 (18)
O2	0.3905 (3)	0.5865 (2)	0.2146 (6)	0.30 (5)	0.376 (11)	0.600 (3)	0.196 (23)
O3	0.2863 (4)	0.8542 (2)	-0.0008 (7)	0.23 (7)	0.304 (11)	0.852 (5)	-0.004 (16)
O4	0.4241 (4)	0.9070 (3)	0.3814 (7)	0.18 (5)	0.434 (10)	0.899 (3)	0.383 (22)
O5	0.6050 (8)	1/2	0.3538 (15)	0.31 (7)	0.623 (10)	1/2	0.400 (28)
O6	0.3908 (8)	1/2	0.6623 (14)	0.38 (6)	0.373 (15)	1/2	0.602 (22)
O7	0.6512 (5)	1/2	0.8405 (9)	0.16 (9)	0.659 (15)	1/2	0.867 (31)
O8	0.1242 (5)	1/2	0.0969 (10)	0.34 (11)	0.140 (0)	1/2	0.055 (32)
O9	0.8940 (7)	1/2	0.3022 (12)	0.14 (10)	0.900 (15)	1/2	0.285 (30)
O10	0.1374 (7)	1/2	0.5840 (13)	0.47 (10)	0.115 (15)	1/2	0.634 (31)
O11	0.6805 (8)	0.6385 (4)	1.0388 (10)	0.51 (6)	0.680 (12)	0.667 (7)	1.076 (23)
C1	0.4704 (5)	0.6937 (4)	0.4620 (10)	0.13 (6)	0.478 (14)	0.694 (3)	0.483 (17)
C2	0.3937 (5)	0.6639 (3)	0.2393 (9)	0.16 (3)	0.398 (11)	0.672 (2)	0.254 (12)
C3	0.3350 (5)	0.7186 (4)	0.0854 (9)	0.25 (2)	0.350 (4)	0.720 (2)	0.062 (5)
C4	0.3394 (5)	0.8021 (4)	0.1281 (9)	0.15 (3)	0.333 (6)	0.797 (2)	0.144 (5)
C5	0.4178 (5)	0.8330 (4)	0.3552 (10)	0.28 (3)	0.402 (5)	0.827 (2)	0.377 (7)
C6	0.4754 (4)	0.7753 (3)	0.5073 (13)	0.18 (5)	0.472 (10)	0.777 (2)	0.535 (16)

the positions between solution and single crystal (in Å<sup>2</sup>) are listed in the last column. The restraints used for the chloranilate ring were taken from the publication of Krogh Andersen (1967).

It can be seen that it is not useful to cut off the data set in the case of powder data. With the whole data set, the solution with the best agreement to the single-crystal solution is clearly that with the best  $R_{wp}$ .

The reason why the refinement became worse with the use of isotropic temperature factors is that the data used ranged only up to 46° in  $\theta$ , with copper X-rays being a result of the geometry of the Guinier diffractometer. Currently, work is in progress to improve this diffraction geometry.

The positions of the solution with the best  $R_{wp}$  of all  $|F|$  are compared with the positions of the single-crystal solution in Table 3, including a value for the distance of the two solutions in the fifth column. The standard deviations of the positions obtained by refinement of the powder data do not represent the actual standard deviations, which are larger. The standard deviations of  $|F|$  are based upon correcting only the Poisson statistics, they do

not include the errors due to the fit and the overlap. Further investigations on suitable weighting schemes have to be performed.

Figs. 2(a) and (b) show plots comparing the single-crystal positions (black dots) with the positions of the solutions achieved by refinement with  $U$  overall and experimental weights (see Table 3), to obtain an overview of the quality of the structural model.

The refinement with the Rietveld program *DBW4.2* shifted the correct positions of some of the atoms significantly, the model therefore became worse (*cf. Brüderl et al., 1994*).

#### 4. Concluding remarks

The results can be summarized as follows:

(a) One of the main problems of a structure determination by powder data is the determination of the space group.

(b) A good weighting scheme for overlapping reflections increases the chances of successful structure determination and also of structural refinement.

(c) Positional refinements with Rietveld programs allow a variety of different results and are therefore a

toothless tool to improve the rough model coming from the direct methods or even the model refined with single-crystal least-squares and restraints. This statement is also confirmed by other authors (Duax, 1993).

(d) Weak reflections are needed for a convergence towards the correct model; it is dangerous to cut off the data set at  $1.5\sigma$ . It is also important to have enough reflections with respect to the number of parameters.

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## Structure of Oxidized Forms of Neodymium and Praseodymium (Bis)phthalocyanines

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#### Abstract

The structure of the tetragonal  $\alpha$ -phase of lanthanide derivatives of (bis)phthalocyanine  $\text{PcL}^{III}\text{Pc}_{\text{ox}}$  ( $\text{Pc} = [\text{C}_{32}\text{H}_{16}\text{N}_8]^{2-}$ ,  $\text{Pc}_{\text{ox}} = [\text{C}_{32}\text{H}_{16}\text{N}_8]^{-}$ , L = lanthanide) crystals is reported. The crystals of  $\text{PcNdPc}_{\text{ox}}$  (I) and  $\text{PcPrPc}_{\text{ox}}$  (II) crystallized on a platinum anode with (I)  $a = 19.544$  (2),  $c = 6.514$  (1) Å,  $Z = 2$ ,  $P4/nnc$ , (II)  $a = 20.066$  (7),  $c = 6.463$  (2) Å,  $Z = 2$ ,  $P4/nnc$ . The structure is built up from columns of equi-distantly separated sandwich-like molecules. The molecular columns are arranged in a regular square lattice,

allowing the stacks to be shifted along the stack axis. The remarkable feature of this structure is the  $\sim 1:2.7$  ratio of the metal-site occupancy coefficients, which is interpreted in terms of a disordered superstructure, the disorder being caused by the presence of a small amount of a triple-decker  $\text{PcLPcLPc}$  complex.

#### Introduction

The lanthanide (bis)phthalocyanine complexes have generated a lot of interest because of their high electrical conductivity (Sullivan, Dominey, Helms,

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