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New achievements in X-ray techniques in the investigations of catalysts

W. Łasocha [a,b,*], A. Rafalska-Łasocha [a], M. Grzywa [b], B. Gaweł [a]

[a] *Faculty of Chemistry, Jagiellonian University, ul. Ingardena 3, 30-060 Krakow, Poland*
[b] *Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, ul. Niezapominajek 8, 30-239 Krakow, Poland*

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Abstract

In recent years great progress has been observed in the field of structure solution from powder data. Structures as complex as 20–30 atoms in an asymmetric unit are solved almost routinely in the semiautomatic black box mode, useful for non-crystallographers. In this paper, as an example of investigations which may be of interest for catalysis, an *ab initio* structure solution of 1,3-phenylenediammonium trimolybdate, solved by a combination of novel XRPD methods, is presented.

Keywords: Catalysts; Powder diffraction; Rietveld refinement

1. Introduction

Environment protection by properly designed chemical treatment of fuels, and industrial wastes to remove polluting elements is now widely adopted, by advantageous utilisation of the unique characteristics of molybdenum catalysts.

The largest, and the most important use of molybdenum catalysts is in the desulphurisation of petroleum and coal derived products. Desulphurisation is employed not only to improve product stability and odour, but most importantly to eliminate sulphur dioxide emission on combustion of fuels, what have a major impact upon air quality [1].

It was found that some molybdates or molybdenum hydrogen bronzes are extremely selective agents for absorption of heavy metals (e.g. actinides), important for water treatment and industrial metal separations. Molybdates can be used for catalytic hydrolytic dehalogenation of halocarbons [2]. It was shown that molybdates can be used also as flame-retardants, corrosion inhibitors and save lubricants.

Substances applied as catalysts are usually multi-component polycrystalline mixtures, almost always with very strong preferred orientation. The most interesting components of catalysts often exist within a narrow range of temperature, pressure and concentration of reagents, as very fine powders suitable only for X-ray powder diffraction techniques.

Besides almost standard phase analysis by the Rietveld method and strain and particle size distribution analysis, powder diffractometry offers today:

- refinement of lattice parameters and crystal structure parameters even in the case of complicated mixtures,
- differentiation between similar elements (e.g. Fe, Ni, Co) by proper choice of wavelengths (possible in synchrotron experiments),
- crystal structure solution of very complex compounds, exceptionally up to 100 atoms in an asymmetric unit,
- structural characterization of amorphous or poorly crystallizing substances [3].

In recent years great progress in the field of powder diffraction data collection (synchrotron sources) and processing (modern computers, new theoretical concepts) has been achieved. Very powerful programs, like EXPO, FOX or DASH [4–6], successfully cope with the crystal structure solution of

* Corresponding author at: Faculty of Chemistry, Jagiellonian University, ul. Ingardena 3, 30-060 Krakow, Poland. Tel.: +48 12 6632053; fax: +48 12 6340515.
E-mail address: lasocha@chemia.uj.edu.pl (W. Łasocha).

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increasingly complicated structures. In the process of structure solution from powders, in addition to increasingly better diffraction data, new approaches exploiting the enormous speed of modern computers and new approaches to building crystal structure models, using genetic algorithm or global optimization techniques, are also used. Moreover, diffraction data are often supported by quantum chemistry calculations and geometric restraints (bond distances and angles). Interestingly, texture – the most serious obstacle in powder diffraction applications to crystal structure study – was recently successfully and actively applied to increase the power and range of applicability of powder diffraction methods [7, Chapter 9].

In our opinion each technique requires a reasonable knowledge of the theoretical background, and black box techniques are often more harmful than profitable. The aim of this paper is neither to teach crystallography, nor to give an overview of dozens of structures solved from powder data. We present here the results of XRPD study of a needle-like powder. Numerous polycrystalline materials are used as catalysts and sometimes they are very poorly characterized since their single crystals are not available. We would like to demonstrate that, from powder data, reliable information about the crystal structure can be found. Successful application of powder diffraction techniques may encourage investigators to further experiments.

2. Experimental

2.1. Synthesis

To a hot solution of $H_2MoO_4 \cdot H_2O$ (0.01 M in 150 ml H_2O), 0.02 M of 1,3-phenylenediamine was added. Next the solution was boiled for 1 h, filtered and left for crystallization at room temperature. After a few days a very fine yellowish-brown powder was precipitated. Chemical analysis indicates that a trimolybdate was obtained. SEM pictures of the obtained material (see Fig. 1) indicate the presence of very thin needles (1 μm × 1 μm × 10 μm), suitable for powder diffraction study only.

2.2. X-ray measurement

Philips X'Pert Pro diffractometer, Cu Kα. Flat sample, reflecting Bragg-Brentano geometry; 2theta range 5–70°. Indexing by Proszki package [8], results of ITO program are listed below as Example 1. Space group: both manual systematic extinction analysis and search using EXPO2004 indicate C2/c (15) as the most probable.

Example 1. 1,3-Phenylenediammonium trimolybdate, result of indexing procedure

A	B	C	ALFA	BETA	GAMMA	VOLUME	FM	L.INDX*
13.3006	**12.6062**	**7.6471**	**90.0000**	**92.9936**	**90.0000**	**1280.44**	**138.8**	**19.**
9.1581	18.3077	5.9741	92.8134	91.0996	92.9325	998.89	11.2	18.
12.7787	13.3660	7.8035	96.5251	99.4816	88.9274	1306.11	8.8	18.
12.6061	13.3054	7.7149	93.3035	90.3375	89.9806	1291.83	8.5	18.

*FM, L.INDX-figure of merit and number of indexed lines (among first 20), accepted solution written in **bold**. Lattice constants after refinement: 13.304(1), 12.607(1) 7.6494(9) Å, 93.016(1)°, V=1281.2(2) Å^3.

Fig. 1. SEM pictures of 1,3-phenylenediammonium trimolybdate.

3. Results

The initial crystal structure model was built using direct methods (EXPO2004) or the charge flipping method. The structure model was completed by the FOX program and refined by the Rietveld method.

3.1. EXPO2004—direct methods package optimized for powder diffraction data [4]

In work connected with the studies of catalysts, we used a very powerful, user-friendly and flexible EXPO package, since nearly all calculations connected with structure solution from powder data (from indexing to Rietveld refinement, with many powerful well-documented options) can be performed using this package.

In particular, using this program package, one can:

- determine lattice parameters and space group by probabilistic approach,
- perform pattern decomposition with automatic background and peak shape selection,

- solve crystal structure by direct methods in semi-automatic, fully *ab initio*, mode,
- insert, if necessary, missing atoms in coordination polyhedra, aromatic rings, etc., automatically,
- refine the structure by the Rietveld method.

In our case the EXPO program detected the presence of a texture with G coefficient and direction 0.38, [1 1 0], respectively. Such information can be used to correct the observed intensities, or to reload the sample using side- or back-loading techniques. We decided to use this information to correct intensities. As a result, in a default run of EXPO, all Mo and O atoms were located. Efforts to locate the organic part, however, were unsuccessful.

Below in Example 2, the input file for EXPO2004 is presented. Such a file is based essentially on the elemental analysis and indexing results. Cell parameters were not refined by EXPO.

Example 2. Input file for EXPO2004

```
range 3.51 69.99 0.02

pattern 13pdak31.pow

cont Mo 12 O 40 C 24 N 8 H 10

wave 1.54184

cell 13.303814 12.607408 7.649443 90.00 93.016 90.00

space C 2/c

nocell
```

3.2. Charge flipping

This method has been elaborated by Oszlányi and Süto [9,10]. Initially it was designed for *ab initio* structure solution from single-crystal data. Very recently Wu et al. [11] and Baerlocher et al. [12] used this method to solve structures from powder diffraction experiments.

The charge flipping algorithm is very simple and robust. In principle it requires only a set of structure factors, amplitudes and cell parameters. Knowledge of space group is not required. Firstly, algorithm generates random phases for each $|F_{h\,k\,l}|$ and a discrete electron density (ED) map **qi** is calculated. Then **qi** is modified by reversing (flipping) the sign of the electron density of all pixels with densities below a given (small) threshold value (d). The major effect is that all negative electron densities are made positive. Then a Fourier transform of this perturbed ED map **qj** is performed and a new set of modified structure factors $G_{h\,k\,l}$ is calculated. The phases of $G_{h\,k\,l}$ are then combined with the experimentally determined amplitudes $|F_{h\,k\,l}|$ for the next iteration. The loop is repeated until convergence or a prescribed number of cycles has been reached.

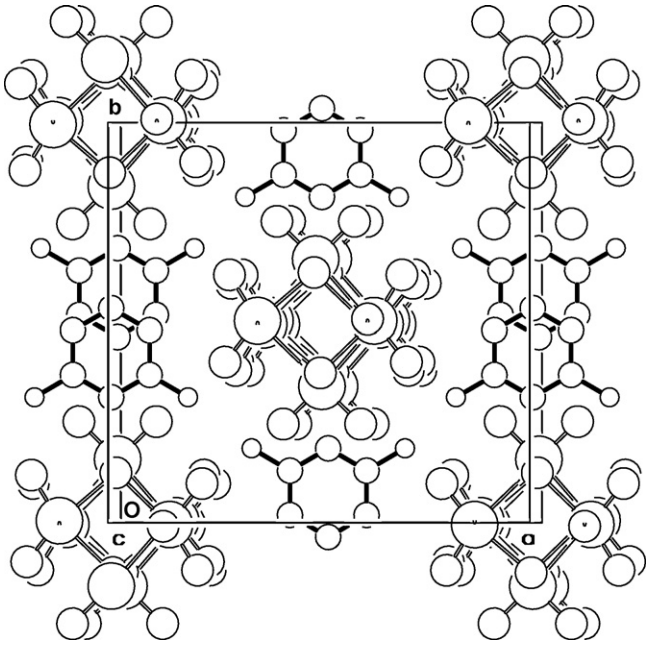

Fig. 2. Projection of the unit cell along [0 0 1]; circles with decreasing radii represent: Mo, O, C and N.

In this work we used the charge flipping algorithm (SUPERFLIP program [13,14]) to solve the structure of the investigated trimolybdate. First we performed Le Bail decomposition using the JANA2000 program [15], and created the input file for the SUPERFLIP program. As a result we obtained an electron density map in which we were able to recognize the polymeric trimolybdate anion responsible for the fibrous morphology.

3.3. Direct space, global optimization methods—FOX program

The FOX program was written for *ab initio* crystal structure determination from X-ray and neutron powder diffraction data. This program uses global-optimization algorithms (simulated annealing or parallel tempering) to find the position and orientation of building blocks in the unit cell. FOX is particularly useful in the case of low-quality diffraction patterns, when building blocks and their connectivity are known, at least approximately. A graphical interface with 3D crystal structure view enables on-line control of the optimization procedure.

Preparation of the input file for the FOX program is rather easy. The main part of the input file consists of a so-called Z-matrix describing the sought molecules in the internal coordination: distances, angles and torsion angles between the atoms. Below in Example 3, a Z-matrix representing 1,3-phenylenediamine is listed.

Example 3. Z-matrix description of 1,3-diphenyleneamine

8	-number of atoms
C 1	-pivot (or anchor) atom
C 1 1.39	-2nd atom and its distance to pivot atom
C 2 1.39 1 120	-3rd atom followed by C3C2 distance and C3C2C1 angle
C 3 1.39 2 120 1 0	-4th atom,C4C3 distance,C4C3C2 angle,C4C3C2C1 torsion
C 4 1.39 3 120 2 0	- etc...
C 5 1.39 4 120 3 0	
N 1 1.35 2 120 3 180	
N 3 1.35 4 120 5 180	

To minimize the work connected with ΔF-Fourier calculations and searching for missing atoms, structure solution was undertaken using EXPO2004 and the charge flipping method. As a result the position and orientation of the Mo–O polymeric anion were found. Next, keeping the positions of Mo and O atoms fixed, the positions and orientation of organic cations were found by the FOX program. Fig. 2 presents the complete structure after the Rietveld refinement.

Table 1
List of atomic parameters (a) and selected interatomic distances (b)

Atom	*x*	*y*	*z*	Uiso
(a)				
Mo1	0.8696(13)	0.9952(18)	1.005(4)	0.016(5)
Mo2	1.0	0.8414(5)	0.75	0.029(11)
O3	0.877(2)	0.991(2)	0.750(5)	0.05(2)
O4	1.093(7)	0.747(8)	0.79(2)	0.03(5)
O5	1.005(10)	0.875(7)	1.046(16)	0.06(5)
O6	0.791(8)	1.098(8)	0.963(18)	0.02(5)
O7	0.803(7)	0.881(5)	1.006(17)	0.05(6)
C1	0.5910(2)	0.019(7)	0.25	0.0539
C3	0.5	0.186(7)	0.25	0.1454
C6	0.5	−0.036(7)	0.25	0.3856
N1	0.6821(4)	0.186(7)	0.25	0.0759

Atom 1	Atom 2	*d*(1–2)
(b)		
Mo1	O3	1.964
Mo1	O3($x,-y,1/2+z$)	1.888
Mo1	O5	2.365
Mo1	O5($-x,-y,-z$)	2.380
Mo1	O6	1.687
Mo1	O7	1.693
Mo2	O3	2.499
Mo2	O3($-x,y,1/2-z$)	2.499
Mo2	O4	1.734
Mo2	O4($-x,y,1/2-z$)	1.734
Mo2	O5	2.303
Mo2	O5($-x,y,1/2-z$)	2.303
N1	O7	2.578

3.4. Rietveld refinement

The crystal structure was refined using the JANA2000 program. This program enables the use of many shapes for diffraction lines, rigid body options, anisotropic broadening of diffraction lines, different texture models and ΔF-Fourier calculations. It can be also used for the study of modulated structures, and to prepare data for external structure solution packages (e.g. EXPO, SUPERFLIP).

The obtained Rietveld plots are presented in Fig. 3, where obtained R factors are also given (in the figure caption). The atomic positions, accompanied by the most interesting Mo–O distances, are listed in Table 1. Fig. 4 presents the investigated structure in polyhedral, ball-and-stick and space filling

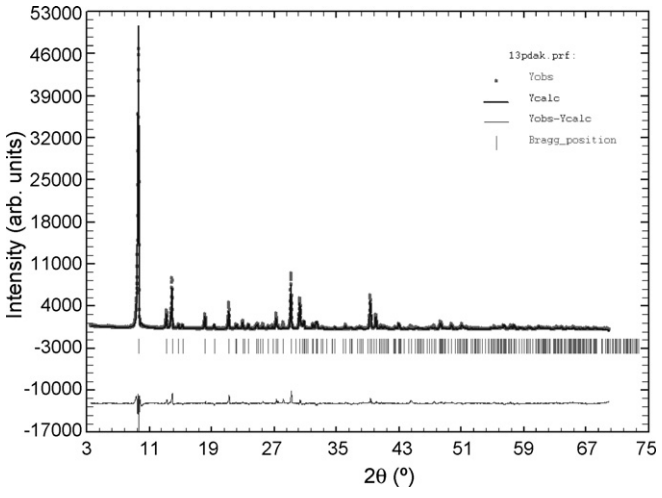

Fig. 3. Rietveld refinement plots, R_{wp} = 16.32%, R_p = 10.9%, R_F = 12.35%.

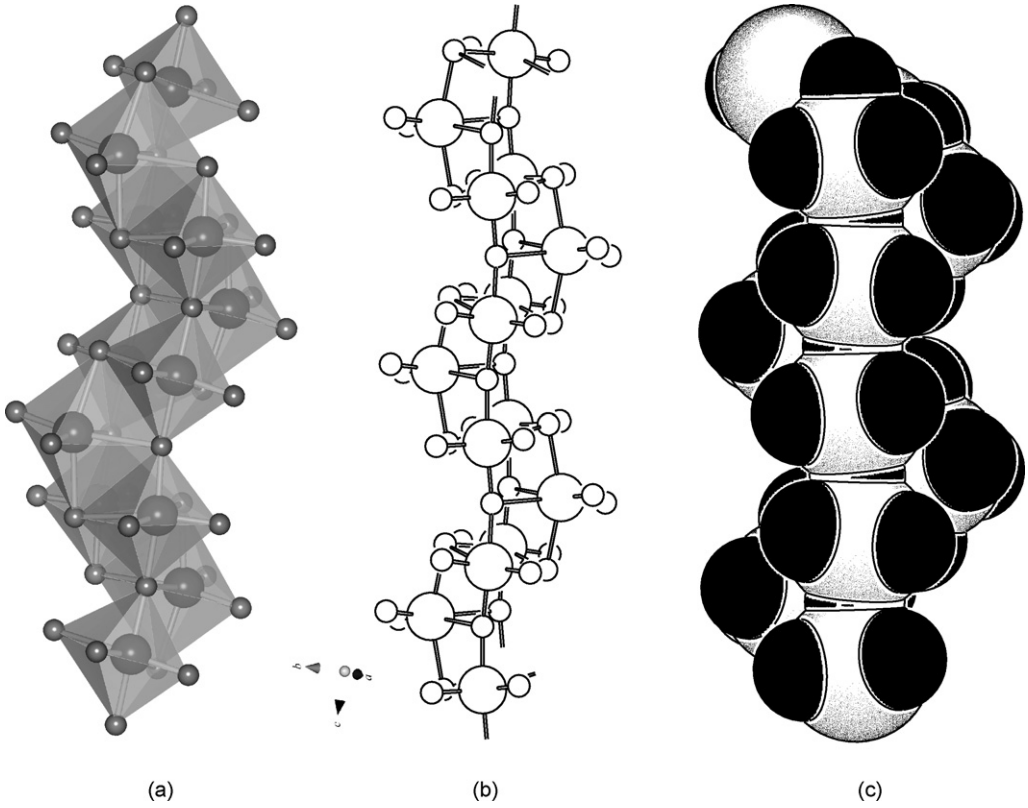

Fig. 4. Anion chain responsible for fibrous morphology in (a) polyhedral, (b) ball-and-stick, (c) space-fill representation.

representations suitable for different types of structure description and interpretation.

3.5. Crystal structure description

The crystal structure consists of parallel, infinite, zigzag chains built up of distorted MoO_6 octahedra. Mo–O distances (reflecting MoO_6 distortion) span a range of 1.689–2.499 Å. By sharing edges and vertices, anionic chains with the general formula $Mo_3O_{10}{}^{2-}$ are created. The same type of anion was observed in many trimolybdates, e.g. $K_2Mo_3O_{10}{\cdot}3H_2O$ [16]. Phenylenediammonium cations are located in the space between chains. Because organic cations (lying on plane (0 0 1)) are exactly parallel to each other, and are placed at a distance of about 3.8 Å from each other, strong π–π interactions are expected between them.

4. Conclusions

Many polycrystalline substances used in catalysis today can be easily investigated by powder diffraction methods, using laboratory X-ray diffractometers. The results of such studies allow for a better characterization of catalytic materials before very sophisticated and expensive methods are applied.

In the study presented, the crystal structure of heretofore unknown 1,3-phenylenediammonium trimolybdate was determined *ab initio* from powder diffraction data, using both direct methods or the very novel 'charge flipping' method. Diffraction data, as well as the input data files for the programs used in the described investigations, can be obtained from the authors on request.

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