

Crystal Structure of Fibrillar Anilinum Trimolybdate $2(\text{C}_6\text{H}_5\text{NH}_3) \cdot \text{Mo}_3\text{O}_{10} \cdot 4\text{H}_2\text{O}$ from X-Ray Powder Data

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Received July 15, 1994; in revised form November 11, 1994; accepted November 13, 1994

The crystal structure of $2(\text{C}_6\text{H}_5\text{NH}_3) \cdot \text{Mo}_3\text{O}_{10} \cdot 4\text{H}_2\text{O}$ was solved *ab initio* from conventional X-ray powder data by the direct method powder diffraction package POWSIM. After three cycles of the intensity-estimating procedure, 18 atoms were found by the direct methods. The remaining atoms were found by difference Fourier and Rietveld methods. The number of atoms in the asymmetry unit was 27; the number of refined parameters, was 78. The structure consists of polymeric chains of Mo-O polyhedra parallel to the *b* axis, surrounded by disordered anilinum cations. Final Rietveld refinement factors are $R_F = 6.1$, $R_{wp} = 17.1\%$, space group *Pnma* (62), $a = 11.0701(7)$, $b = 7.6131(7)$, $c = 25,550(5)$ Å, and $Z = 4$. © 1995 Academic Press, Inc.

INTRODUCTION

The main obstacle to structure solution from powder diffraction data is the problem of overlapping reflections. Despite many theoretical achievements in this field (1-4), the most complicated structures solved from powder data up to now (5, 6) have been solved, according to Le Bail (6), by the "brute force method." Brute force in this context implies pattern decomposition with a very small separation limit (e.g., 0.04° in 2θ), then solving the structure using data only from the decomposition program. The very incomplete structural models, usually including only heavy atoms, are successively refined and completed by a sequence of Rietveld refinements and Fourier map calculations. Both complex structures, that Le Bail mentioned consist of 29 atoms, the first structure being solved from synchrotron dates, the second from conventional X-ray powder data.

Recently we started the structural investigation of a family of fibrillar crystals using direct methods (3) to solve the problem of overlapping reflections. The structures of these compounds were unknown and could be investi-

gated only by powder diffraction methods because of the fibrillar nature of the crystals. Using the direct methods powder diffraction package POWSIM (3, 7, 8), we solved the crystal structure of silver, potassium, and ammonium fibrillar trimolybdates (9-11).

We report here the results for the crystal structure solution of anilinum trimolybdate, the most complicated structure in this family of compounds, a structure with 27 atoms in the asymmetric unit. An intensity-estimating procedure based on direct methods allowed the straightforward location of 18 atoms by the structure solution program SIMPEL (8). The results obtained clearly indicate the potential of the method we used. In our work we use X-ray data collected with a conventional powder diffractometer.

DATA COLLECTION AND SPACE GROUP DETERMINATION

The sample, prepared according to the published procedure (12), was ground under alcohol and loaded into a specimen holder from the back side to avoid texture as much as possible. Two divergence slits were used, 0.25° and 1° , for measurement below and above $2\theta = 20^\circ$, respectively. Further details of the data collection are presented in Table 1.

The lattice parameters as determined in previous work (11) were used in both structure determination and refinement. From an analysis of the systematic extinctions the lattice type was determined as "P" and the presence of a symmetry center was assumed. However, due to large lattice parameters (e.g., $c = 25,550(2)$ Å), it was not possible to determine the space group unambiguously. The program SPACE (13) indicated "pseudo-centering" of *B* or *I* type. The lattice parameter *b* and the morphology suggest similarities of anilinum trimolybdate to other trimolybdates (9-11); in all of them the length of the poly-

TABLE 1
Details of Data Collection and Structure Refinement
 $2(\text{C}_6\text{H}_5\text{NH}_3) \cdot \text{Mo}_3\text{O}_{10} \cdot 4\text{H}_2\text{O}$

Diffractometer	PW3710 Philips X'pert
Radiation	$\text{CuK}\alpha$, filtered
2θ range ($^\circ$)	6–96
Step scan increment ($^\circ$)	0.02
Count time (sec/step)	18
Standard peak: hkl , 2θ ($^\circ$)	110, 8.716
R for standard peak (%)	0.9%
Space group	$Pnma$ (62)
a (\AA)	11.0701 (7)
b (\AA)	7.6131 (7)
c (\AA)	25.550 (2)
V (\AA^3)	2153.3 (5)
Number of observations	4101
Number of reflections	964
Number of structural parameters refined	78
Number of profile parameters refined	9
R_F (%)	6.6
R_I (%)	9.6
R_{wp} (%)	17.1
R_{exp} (%)	6.7
Max shift/error	0.3

meric unit is about 7.57 \AA . Since the symmetry of the polymeric anion of nearly all known trimolybdates is $2_1/m$, only space groups allowing such symmetry were considered. Cell contents and the above information indicate the space group $Pnma$ (62) as being the most probable one.

INTENSITY ESTIMATION AND STRUCTURE SOLUTION

The procedures and the organization of the POWSIM System have been extensively described in the original papers (3, 7, 8); the solutions of unknown structures obtained using this package are described in our previous papers (9–11).

For the structure solution only part of the diffraction pattern, up to $65^\circ 2\theta$, was used; 435 peaks were possible in this range. The diffraction pattern was decomposed for single and overlapping intensities by the LSQPROF program, with an R value of 5.24%.

The DOREES program for estimating the overlapping reflections from the nonoverlapping ones, using Patterson and direct method criteria, provides the option of influencing the unraveling strategy. As a matter of fact, the program defaults are not fully established since POWSIM has as yet been applied only to a limited number of structures. As a result, the first two trials, consisting of intensity estimation and structure solution, failed. In both, the Patterson information for estimating intensities from overlapping sum-intensities was excluded. The third trial included a criterion by which to judge the division of sum-intensities in individual cases based on the Patterson function and prove to be much more successful, revealing

straightforwardly 2/3 of the structure. In a successful trial, the peak separation limit was 0.333 FWHM (FWHM represents the full width at half-maximum), the weights of Patterson function and each direct method criterion were 1 and 0.5, respectively. After three cycles of DOREES intensity estimation, the group of uniquely determined intensities contained 226 reflections, that is, 52% of the total number of reflections and 71 $E_s \geq 1.0$ (53% of all $E_s \geq 1$). The strongest 75 E_s were used by SIMPEL88, and in the resulting E -map can be found not only most atoms of the Mo–O chain, but also one distorted benzene ring and a big part of the other.

RIETVELD REFINEMENT OF THE STRUCTURE

The structure was completed and further refined by the Rietveld method using the PC version of XRS-82 (14). It was found that in the centrosymmetric space group $Pnma$, phenyl rings, not lying in the $x0.25z$ plane, must be disordered (with sof 0.5) to avoid superimposing with symmetry equivalent rings, or symmetry should be lowered to $Pn2_1a$. At first a disordered model was tested.

$Pnma$ —Centrosymmetric Space Group

The structure was very difficult to refine; constrained refinement was only possible for the pattern corrected by the LP factor. Similar problems were encountered in the refinement of the ammonium trimolybdate structure. Also, in that case, LP correction of the pattern prior to Rietveld refinement improved the stability of the refinement (11). Initially only part of the pattern was used: that from 10° to 70° . The peak range was limited to 3 HRFM. First, molybdenum–oxygen chains were refined; then by difference Fourier methods, missing atoms in phenyl rings atoms were found. In next refinement cycles, two phenyl rings were included in the refinement process. Then, two nitrogen atoms and one water molecule were located. The overall temperature factor, preferred orientation factor, and 68 parameters for 24 atoms were refined in full matrix mode, giving R_F and R_{wp} factors of 9.4 and 19.4. The weight of the geometric constraints was 20% of that of the diffraction data.

After all diffraction data were included, three water molecules were found. However, in this case full-matrix refinement of all parameters required higher weights of geometric observations. Particularly responsible for the decreasing stability of refinement is the strong 002 reflection observed at 2θ 6.96° . The intensity observed for this reflection is smaller than the calculated value. Using samples kept in a desiccator over P_2O_5 , it has been observed recently that the intensity of the 002 line is particularly sensitive to water content. This can be explained because the z coordinates of all water molecules are close to 0.25

TABLE 2
List of Atomic Parameters

Atom	x	y	z	U	sof
Mo(1)	0.499(2)	0.493(2)	0.0708(2)	0.013(1)	
Mo(2)	0.3191(6)	0.2500	-0.0050(4)	0.008(2)	
O(1)	0.390(4)	0.542(8)	0.119(2)	0.002(5)	
O(2)	0.634(3)	0.49(1)	0.110(2)	0.002	
O(3)	0.382(2)	0.491(7)	-0.004(2)	0.002	
O(4)	0.484(6)	0.2500	0.072(2)	0.002	
O(5)	0.476(6)	0.2500	-0.049(2)	0.002	
O(6)	0.210(5)	0.2500	0.048(2)	0.002	
O(7)	0.229(5)	0.2500	-0.060(2)	0.002	
N(1)	0.79(1)	0.2500	0.005(7)	0.02	
N(2)	0.19(1)	0.7500	0.139(4)	0.01	
C(1)	0.84(2)	0.07(2)	0.132(6)	0.02(2)	0.5
C(2)	0.93(2)	-0.06(2)	0.121(6)	0.02	0.5
C(3)	0.98(1)	-0.07(2)	0.072(7)	0.02	0.5
C(4)	0.94(1)	0.04(2)	0.033(5)	0.02	0.5
C(5)	0.85(2)	0.16(2)	0.046(4)	0.02	0.5
C(6)	0.83(2)	0.19(2)	0.100(6)	0.02	0.5
C(11)	-0.05(1)	0.40(2)	0.205(6)	0.01(2)	0.5
C(12)	-0.01(1)	0.37(2)	0.154(5)	0.01	0.5
C(13)	0.10(1)	0.47(1)	0.137(5)	0.01	0.5
C(14)	0.14(1)	0.62(2)	0.166(4)	0.01	0.5
C(15)	0.07(1)	0.66(2)	0.215(3)	0.01	0.5
C(16)	-0.02(1)	0.56(2)	0.231(4)	0.01	0.5
O(11) ^a	0.24(1)	0.2500	0.771(6)	0.13(3)	
O(12)	0.88(1)	0.2500	0.285(6)	0.13	
O(13)	0.19(2)	0.2500	0.213(6)	0.13	
O(14)	0.115(7)	0.2500	0.714(4)	0.13	

^aO(11)–O(14) represent water molecules.

TABLE 3
Selected Interatomic Distances

Mo(1)–O(1)	1.77	(5)	Mo(2)–O(7)	1.73	(5)
O(2)	1.79	(4)	O(6)	1.82	(6)
O(4)	1.86	(2)	O(3)	1.96	(5)
O(5)	2.05	(2)	O(3)	1.96	(5)
O(3)	2.17	(5)	O(5)	2.07	(6)
O(3)	2.30	(5)	O(4)	2.68	(6)

or 0.75, so the number of water molecules can change the intensity of the 002 reflection. Unfortunately, this fact was not known during data collection and sample preparation for elementary analysis, so special precautions to avoid a change in water amount were not undertaken.

Final refinement was performed in three runs; in the first run, atoms of Mo–O chains were refined, in the second, phenyl rings, in the third run, water molecules and profile parameters. Final discrepancy factors are $R_F = 6.1$, $R_I = 9.6$, and $R_{wp} = 17.1$.

Pn2₁a—Noncentrosymmetric Space Group

The same procedures, data sets, and constraints, adapted to space group *Pn2₁a*, were used in Rietveld refinement. Discrepancy factors were slightly higher than in the space group *Pnma*. In addition, the common temperature factor for all oxygen atoms was refined to a negative value, and the geometry of the Mo–O chains

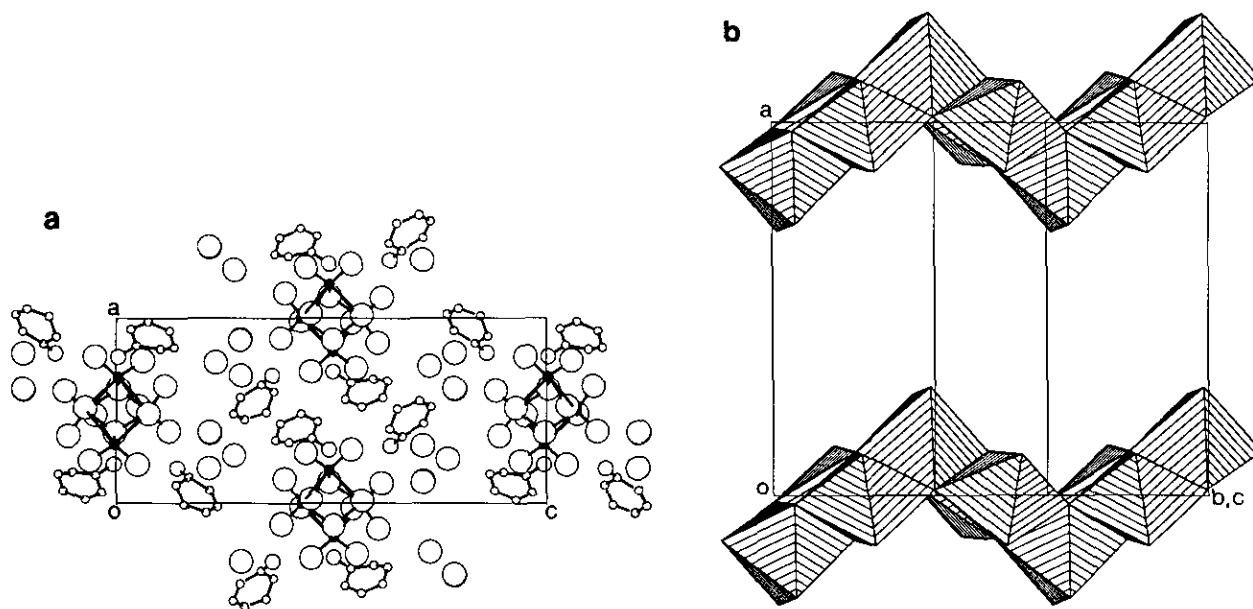


FIG. 1. (a) Projection of the structure of $2(C_6H_5NH_2) \cdot Mo_7O_{10} \cdot 4H_2O$ along the *b* axis. The large, medium, small, and small-black circles represent oxygen, nitrogen, carbon, and molybdenum atoms, respectively. (b) Parallel Mo–O chains in polyhedral representation.

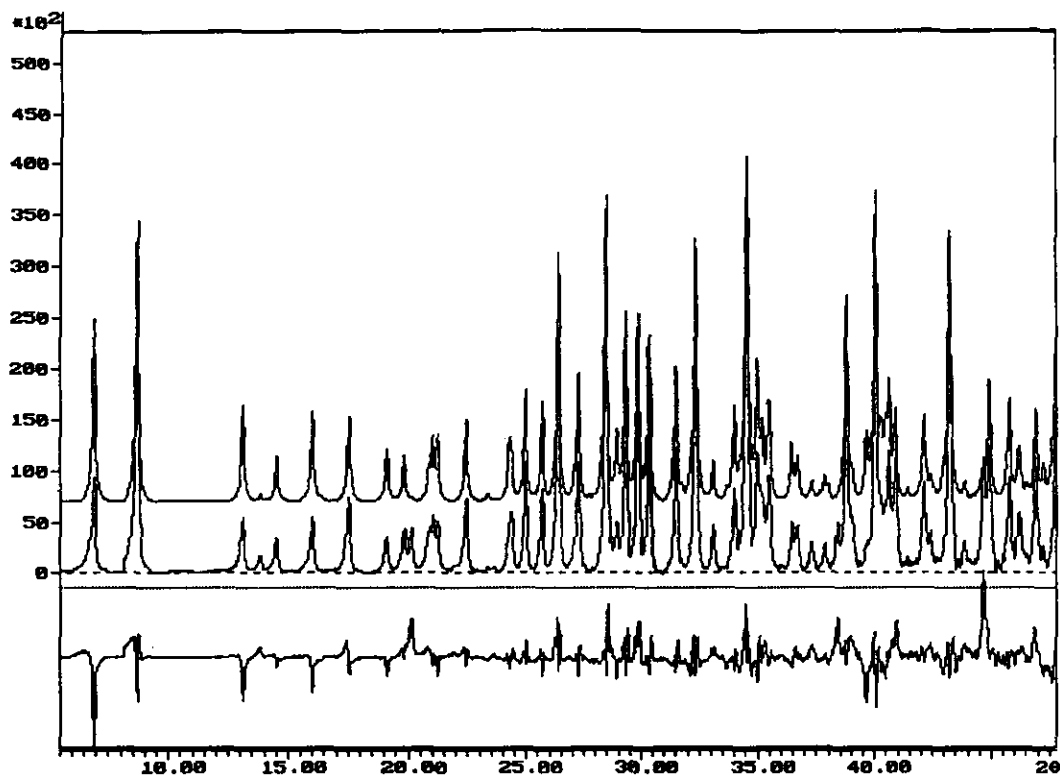


FIG. 2. Observed (middle), calculated (upper), and difference (lower) profiles for the Rietveld refinement of $2(\text{C}_6\text{H}_5\text{NH}_3) \cdot \text{Mo}_3\text{O}_{10} \cdot 4\text{H}_2\text{O}$.

was definitely worse. So these structural results also indicate that the space group is *Pnma*.

STRUCTURE DESCRIPTION AND DISCUSSION

The structure consists of infinite zigzag chains of distorted edge-shared MoO_6 octahedra lying parallel to the *b* axis. The same type of molybdenum–oxygen chains were found in rubidium, silver, potassium, and two forms of ammonium trimolybdates (9–11, 16, 17). The distortions present in the MoO_6 octahedra are reflected by the bond-length variation, the Mo–O distances being between 1.77–2.30 Å for one type of molybdenum atom and 1.73–2.68 Å for the other. As in most structures built up from MoO_6 octahedra, the shortest Mo–O distances are observed for the terminal bonds, these bonds being in the *cis* position. Adjacent chains have no common oxygen atoms and are held together by a system of hydrogen bonds formed by water molecules. Mo–O chains are surrounded by anilinium cations forming hydrophobic regions; disordered water molecules form hydrophilic layers in positions *x*, *y*, ~ 0.25 . The average C–C and C–N distances are 1.40(19) and 1.38(16) Å. The precision of the atom positions is rather low, but a large esd can be expected for such a complicated structure, and also the esd's of atomic positions and bond distances were calcu-

lated according to Scott (15), so they are a few times higher than that reported by other Rietveld programs. The final atomic parameters and most important interatomic distances in Mo–O chains are listed in Tables 2 and 3. Figure 1 illustrates the projection of the structure along the *b* axis. The observed, calculated, and difference patterns are presented in Fig. 2. The final Rietveld plots for the case of the pattern corrected by LP are noisier than the normal pattern, but the *R* factors are convincing enough, in our opinion. It should be stressed that the LP factor can obscure even large differences between F_o and F_c because in the high angular range (e.g., $2\theta \geq 60^\circ$), observed intensities are very small and the difference pattern looks accordingly flattened. Except for the title compound, only one anilinium molybdate, β -octamolybdate, has been described (18). Its structure consists of discrete, well-known $\beta\text{-Mo}_8\text{O}_{42}^{4-}$ units built up of distorted octahedra.

CONCLUSIONS

—Applied methods allow the structure solution of a 27-atom structure to be achieved. The criterion for judging the division of sum-intensities into individual ones based on the Patterson function can be essential when the default approach fails. Such an approach is recommended when

expected interatomic vectors can be discerned in the Patterson map (note that the Patterson map need not be interpreted).

—In the case of complicated structures, similarities with known structures and chemical sense of solution should be sought as additional confirmation of the structure solution.

—Geometric constraints and removal of the Lorentz–polarization component from the diffraction pattern increase the stability of the Rietveld refinement.

The title compound and the programs used will be the subject of further tests with better diffraction data, e.g., synchrotron or neutron radiation.

ACKNOWLEDGMENTS

The support of the Polish Committee of Science Research (KBN 0096/P3/93/05) and the Foundation of Crystallographic Studies through a Carolina H. MacGillary stipend is kindly acknowledged.

REFERENCES

1. M. Tremayne, P. Lightfoot, C. J. Gilmore, and G. Bricogne, *J. Solid State Chem.* **100**, 191 (1992).
2. M. A. Esterman, L. B. McCusker, and C. Baerlocher, *J. Appl. Crystallogr.* **25**, 539 (1992).
3. J. Jansen, R. Peschar, and H. Schenk, *J. Appl. Crystallogr.* **25**, 237 (1992).
4. G. Cascarano, L. Favia, and C. Giacovazzo, *J. Appl. Crystallogr.* **25**, 310 (1992).
5. R. E. Morris, W. T. A. Harrison, J. M. Nicol, A. P. Wilkinson, and A. K. Cheetham, *Nature* **359**, 519 (1992).
6. A. Le Bail, *J. Solid State Chem.* **103**, 287 (1993).
7. J. Jansen, R. Peschar, and H. Schenk, *J. Appl. Crystallogr.* **25**, 231 (1992).
8. J. Jansen, R. Peschar, and H. Schenk, *Z. Kristallogr.* **206**, 33 (1993).
9. W. Lasocha, J. Jansen, and H. Schenk, *J. Solid State Chem.* **109**, 1 (1994).
10. W. Lasocha, J. Jansen, and H. Schenk, *J. Solid State Chem.*, to appear.
11. W. Lasocha, J. Jansen, and H. Schenk, *J. Solid State Chem.*, to appear.
12. W. Lasocha, J. Janczur, and S. A. Hodorowicz, *Pol. J. Chem.* **67**, 1027 (1993).
13. "Program Space," Lab. v. Kristallographie, Universiteit van Amsterdam. Local program.
14. Ch. Baerlocher, "XRS-82. The X-ray Rietveld System." Institut für Kristallographie, Eidgenössische Technische Hochschule, Zurich, Switzerland (1982); PC version of XRS: D. Mucha and W. Lasocha, *J. Appl. Crystallogr.* **27**, 201 (1994).
15. H. G. Scott, *J. Appl. Crystallogr.* **16**, 159 (1983).
16. H. U. Kreusler, A. Foerster, and J. Fuchs, *Z. Naturforsch. B* **35**, 242 (1980).
17. K. J. Range and A. Faessler, *Acta Crystallogr. C* **46**, 488 (1990).
18. P. Roman, J. M. Gutierrez-Zorrilla, C. Esteban-Calderon, M. Martinez-Rippol, and S. Garcia-Blanco, *Polyhedron* **4**, 1043 (1985).