

Table 2. *Interatomic distances (Å) and angles (°)*

Sr—Sr ⁱⁱ	3.99 (6)	Sr—Sr ⁱⁱⁱ	3.76 (6)
Sr—Sr ⁱⁱⁱ	3.48 (6)	Sr—Cu(2)	3.25 (4)
Sr—Cu(3)	3.2 (1)	Sr—Cu(3')	3.80 (4)
Sr—O(2)	2.5 (2)	Sr—O(3)	2.78 (8)
Sr—O(5)	2.0 (4)	Sr ⁱ —Sr ⁱⁱ	3.79 (6)
Sr ⁱ —Cu(3')	3.79 (5)	Sr ⁱ —O(5')	2.5 (5)
Sr ⁱⁱ —Cu(3')	3.16 (5)	Sr ⁱⁱ —O(5)	2.8 (5)
Sr ⁱⁱ —O(5')	2.4 (3)	Sr ⁱⁱⁱ —Cu(2)	3.22 (4)
Sr ⁱⁱⁱ —O(2)	2.8 (2)	Sr ⁱⁱⁱ —O(3)	2.39 (8)
Cu(1)—Cu(2)	2.765 (8)	Cu(1)—O(1)	1.970 (3)
Cu(1)—O(2)	1.91 (4)	Cu(2)—O(1)	1.85 (4)
Cu(2)—O(2)	1.97 (1)	Cu(2)—O(3)	2.00 (3)
Cu(3)—Cu(3')	2.739 (8)	Cu(3)—O(4)	1.92 (3)
Cu(3)—O(5)	1.9 (2)	Cu(3')—O(4)	1.79 (3)
Cu(3')—O(4')	1.92 (3)	Cu(3')—O(5)	2.0 (2)
Cu(3')—O(5')	1.82 (9)	O(1)—O(2)	2.68 (4)
O(2)—O(3)	2.84 (4)	O(4)—O(4')	2.76 (4)
O(4)—O(5)	2.6 (2)	O(4')—O(5')	2.6 (1)
O(5)—O(5')	2.8 (2)		
O(1)—Cu(1)—O(2)	87. (1)	O(1)—Cu(2)—O(2)	89. (1)
O(2)—Cu(2)—O(3)	91. (1)	O(4)—Cu(3)—O(5)	87. (3)
O(4)—Cu(3')—O(4')	96. (1)	O(4)—Cu(3')—O(5)	86. (3)
O(4')—Cu(3')—O(5')	87. (3)	O(5)—Cu(3')—O(5')	94. (5)
Cu(1)—O(1)—Cu(2)	93. (1)	Cu(1)—O(2)—Cu(2)	91. (1)
Cu(3)—O(4)—Cu(3')	95. (1)	Cu(3)—O(5)—Cu(3')	90. (9)

Symmetry code: (i) $x, y, z + 1$; (ii) $x, -y + \frac{1}{2}, z + \frac{1}{2}$; (iii) $x, -y, z$.

Several structural studies on very closely related materials have been reported: $(\text{Sr}_{14-x}\text{Ca}_x)\text{Cu}_{24}\text{O}_{41}$ ($0 < x \leq 8$) (McCarron *et al.*, 1988); $M_{10}\text{Cu}_{17}\text{O}_{29}$ ($M = \text{Bi}_{0.031}\text{Ca}_{0.564}\text{Sr}_{0.405}$) (Kato, 1990); $(\text{Sr}, \text{Ca})_{14}\text{Cu}_{24}\text{O}_{41}$ (Milat, van Tendeloo, Amelinckx, Mehdob & Deltour, 1992). As found by McCarron *et al.* in the Ca-free compound, adjacent $(\text{CuO}_2)_\infty$ chains are staggered along the c axis and a face-centred lattice is not formed in the second subsystem unlike the Ca-

containing compounds. In the TEM study (Milat *et al.*, 1992), diffuse intensity planes perpendicular to the c^* axis were observed in the second subsystem, which indicate the positional disorder in the successive rows of $(\text{CuO}_2)_\infty$ chains. The precession photographs of our samples were taken perpendicular to the b^* axis (Shishido *et al.*, 1992) and none of the aforementioned streaks were visible.

We thank A. Yamamoto (National Institute for Research in Inorganic Materials) for useful suggestions concerning symmetry. Our thanks are also due to A. Sayama and F. Iwase (Furukawa Electric Co.) for EPMA analysis and Y. Watanabe for step-scan measurements. We are grateful to M. Onoda (National Institute for Research in Inorganic Materials) for information about the structural study of this compound.

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Acta Cryst. (1994). **B50**, 45–50

Experiences with a Structure Determination on the Basis of Powder Data

BY G. BRÜDERL, H. BURZLAFF,* W. ROTHAMMEL, R. SPENGLER AND H. ZIMMERMANN

Institut für Angewandte Physik, Lehrstuhl für Kristallographie, Bismarckstrasse 10, D-91054 Erlangen, Germany

AND B. PERDIKATSIS

Institute of Geology and Mineral Exploration, Messogion 70, 11527 Athens, Greece

(Received 18 February 1993; accepted 16 August 1993)

Abstract

The result of a crystal structure determination on the basis of Guinier powder data is compared with the structure based on single-crystal data. Both determinations agree roughly regarding the arrangement

of the atoms; however, the powder-data result shows strong deviations with respect to the correct atomic positions.

Introduction

In connection with the problem of characterization of a series of alanates, the authors were confronted

* To whom correspondence should be addressed.

with the structure determination of these compounds. Since some of them were not available as single-crystal specimens the structure determination could only be performed with powder data. For testing the reliability of powder-data investigations of this type the results of the structure determination for $\text{UO}_2(\text{C}_6\text{O}_4\text{Cl}_2)_2\text{Na}_2 \cdot 6\text{H}_2\text{O}$ on the basis of single-crystal data (Bram, Brüderl, Burzlaff, Karayannis, Lange & Spengler, 1994) will be compared with the structure derived from a suitable powder data set, Fig. 1.

Data collection and derivation of intensities

The lattice parameters of the sample could be determined with Guinier powder data as monoclinic I with $a_p = 12.2164$ (3), $b_p = 16.5388$ (4), $c_p = 5.9181$ (2) Å and $\beta_p = 102.568$ (2)°.

To localize the well resolved powder lines, the graphic part of the program system *DIFFRAC/AT* (Siemens, 1993) was applied. For indexing, the program of Visser (1969) was used. No special extinctions could be recognized, thus the allowed space groups are $I2/m$, $I2$ and Im . These results are in good agreement with the single-crystal data: $a_{sc} = 12.188$ (2), $b_{sc} = 16.518$ (3), $c_{sc} = 5.908$ (1) Å and $\beta_{sc} = 102.57$ (1)°; space group Im .

There are 527 reflections in the range $0 \leq \sin\theta/\lambda \leq 0.47 \text{ \AA}^{-1}$. To avoid overlapping as far as possible the Guinier technique was chosen to be most suitable for the data collection. The instrument used was a Huber Guinier diffractometer with diameter 114.6 mm, focusing Johansson monochromator [Ge(111)] and a soller slit unit in front of the sample. The instrument was equipped with a scintillation counter. The apparatus was modified with respect to (i) the driving motor – instead of a synchronous motor, a stepping motor under the control of a PC was used; (ii) the sample mounting device – to diminish texture and grain-size influences a rotating sample mounting device was installed (Brüderl, Burzlaff & Perdikatsis, 1994). The measurement was performed in asymmetric transmission geometry ($\psi = 45^\circ$) with $\text{Cu K}\alpha_1$ radiation, 2° primary-beam aperture, detector slit width of 0.04 mm and slit height of 8.0 mm. The range of observation was $6.0 \leq 2\theta \leq$

92.0° with a step width of 0.01° for 2θ . The counting time per step was 3 s. To improve the counting statistics the observation range was measured 20 times. The rotation frequency of the sample was selected to be 5 Hz. So the total measuring time was 6 days.

To increase the resolution a special whole-pattern-fit program was developed. Powder lines with a smaller distance than $\frac{1}{3}$ of the full width at half-maximum (FWHM) [in this case 0.03° (2θ)] from each other were considered unresolvable thus producing one single peak. In this case 206 reflections were affected by this condition. For each group of overlapping reflections, the reflection with the smallest 2θ angle was regarded as being representative. Thus the whole pattern was separated into 321 resolved lines and 95 overlapping groups. In the fitting procedure the resolved peaks and one representative of each group were fitted. The group intensity was distributed uniformly among the number of overlapping reflections taking into account the multiplicity of the reflection.

For the profile-fitting procedure the well known formula for the calculation of powder intensities via a profile shape function (PSF) was applied. The fitting process minimizes

$$R = \sum_{m=1}^M [1/I_{\text{obs}}(\theta_m)][I_{\text{obs}}(\theta_m) - I_{\text{calc}}(\theta_m)]^2$$

$$I_{\text{calc}}(\theta_m) = \sum_{n=1}^N I_0(\theta_n) \text{PSF}(\theta_m, \theta_n, U, V, W) \text{ASP}(\theta_m, \theta_n) - \sum_{l=-1}^L b_l \theta_m^l,$$

with M the number of measurement steps; N the number of fitted lines; θ_n the Bragg angle for diffraction line n , corrected for errors, resulting from sample displacement; $I_{\text{obs}}(\theta_m)$ [$I_{\text{calc}}(\theta_m)$] the observed (calculated) intensity at the diffraction angle θ_m ; $I_0(\theta_n)$ the calculated height of the peak at position θ_n ; $\text{PSF}(\theta_m, \theta_n, U, V, W)$ the profile shape function (here the pseudo-Voigt function); U, V, W the profile shape function parameters describing the dependence of FWHM^2 of θ_m as used by Rietveld (1969); $\text{ASP}(\theta_m, \theta_n)$ the asymmetry correction due to the instrumental geometry for small angles θ_m ($2\theta_m \leq 30^\circ$); b_l the coefficients of a background polynomial of order L ; and θ_m the Bragg angle at the m th measurement step.

For the refinement, a Levenberg–Marquardt algorithm (Press, Flannery, Teukolsky & Vetterling, 1992) was used. The refinement process runs in alternating steps, similar to the method described by Jansen, Peschar & Schenk (1992). First background parameters, the specimen displacement parameter and parameters concerning the profile shape were refined; in the following step only the peak heights

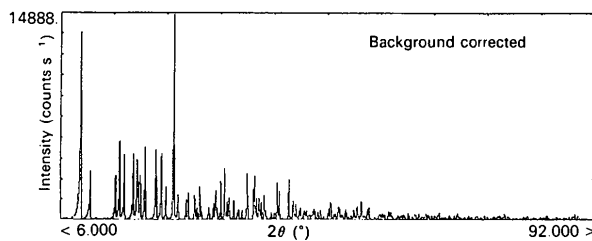


Fig. 1. Diffraction pattern of $\text{UO}_2(\text{C}_6\text{O}_4\text{Cl}_2)_2\text{Na}_2 \cdot 6\text{H}_2\text{O}$.

Table 1. *Atomic coordinates and comparative distances*

All comparisons refer to the refinement results of the single-crystal investigation (Bram, Brüderl, Burzlaff, Karayannis, Lange & Spengler, 1994). These coordinates are given in columns 2–4, line 1; line 2 contains coordinates derived from the single-crystal Patterson function; line 3 those derived from the powder Patterson function; column 5 gives the Patterson weights (single-crystal data above, powder data below) and columns 6–9 show the comparative distances.

	<i>x</i>	<i>y</i>	<i>z</i>	Patterson weights:		Distances (Å)			
				single crystal	powder	d_{Patisc}	d_{Riet}	d_{mrf}	d_{qsc}
U	0.0000	0.0000	0.0000						
Cl3	0.7480 (1)	0.1820 (1)	0.3311 (2)						
	0.7495	0.1822	0.3300	15.6	0.02				
	0.7495	0.1732	0.3414	11.1	0.16	0.08	0.13	0.08	
Cl6	0.5599 (1)	0.1997 (1)	0.7651 (3)						
	−0.4376	0.1901	−0.2383	13.8	0.04				
	−0.4317	0.1850	−0.2482	10.8	0.17	0.10	0.15	0.05	
Na1	0.7751 (2)	0.0000	0.4199 (5)						
	0.7798	0.0000	0.4206	12.6	0.06				
	0.7776	0.0000	0.4245	12.1	0.03	0.15	0.09	0.01	
Na2	0.3088 (3)	0.0000	0.1098 (5)						
	0.3104	0.0000	0.1040	10.4	0.04				
	0.3070	0.0000	0.1379	7.3	0.17	0.50	0.10	0.13	
O1	0.0229 (3)	0.1394 (2)	0.0852 (6)						
	0.0287	0.1362	0.0932	8.8	0.09				
	0.0371	0.1506	0.1162	10.3	0.12	0.37	0.25	0.28	
O2	0.8905 (3)	0.0865 (2)	0.7146 (6)						
	−0.1030	0.0858	−0.2679	8.9	0.12				
	−0.1082	0.1029	−0.3140	6.8	0.32	0.42	0.16	0.06	
O4	0.2863 (3)	0.1458 (2)	0.9993 (6)						
	−0.7101	0.1412	−0.0113	7.9	0.11				
	−0.6938	0.1415	−0.0620	7.2	0.48	0.17	0.29	0.37	
O5	0.4241 (4)	0.0930 (2)	0.3814 (7)						
	0.4262	0.0913	0.3860	8.2	0.04				
	0.4383	0.0993	0.4020	7.5	0.22	0.29	0.28	0.19	
O11	0.1050 (8)	0.0000	0.8538 (15)						
	−0.8871	0.0000	−0.1582	11.1	0.13				
	−0.9032	0.0000	−0.1280	13.1	0.16	0.50	0.09	0.44	
O12	0.8908 (7)	0.0000	0.1623 (14)						
	0.8871	0.0000	0.1582	11.1	0.05				
	0.9032	0.0000	0.1280	13.1	0.28	0.45	0.25	0.20	
O21	0.1512 (5)	0.0000	0.3405 (9)						
	0.1440	0.0000	0.3393	7.8	0.09				
	0.1529	0.0000	0.3667	8.1	0.15	0.29	0.09	0.20	
O22	0.6242 (5)	0.0000	0.5969 (10)						
	−0.3766	0.0000	−0.3983	6.8	0.03				
	−0.3475	0.0000	−0.4193	6.6	0.38	0.30	0.33	0.27	
O23	0.3940 (6)	0.0000	0.8022 (12)						
	−0.6319	0.0000	−0.1036	7.2	0.41				
	−0.6267	0.0000	−0.1583	7.9	0.12	0.49	0.18	0.09	
O24	0.6374 (6)	0.0000	0.0840 (13)						
	0.6319	0.0000	0.1036	7.2	0.14				
	0.6267	0.0000	0.1583	7.9	0.48	0.42	0.42	0.28	
O25	0.1805 (8)	0.1385 (4)	0.5388 (10)						
	−0.8258	0.1418	−0.4739	6.6	0.11				
	−0.8262	0.1480	−0.4821	7.7	0.20	0.06	0.29	0.19	
C1	0.9704 (4)	0.1937 (3)	0.9620 (9)						
	−0.0253	0.1850	−0.0617	7.4	0.21				
	−0.0582	0.2091	−0.0234	6.0	0.45	0.25	0.54	0.44	
C2	0.8936 (4)	0.1639 (4)	0.7399 (8)						
	−0.1001	0.1631	−0.2536	8.1	0.08				
	−0.1179	0.1777	−0.2673	7.4	0.27	0.55	0.13	0.26	
C3	0.8350 (5)	0.2186 (3)	0.5854 (9)						
	−0.1627	0.2197	−0.4234	6.7	0.08				
	−0.1930	0.2139	−0.4169	6.2	0.35	0.15	0.24	0.30	

Table 1 (cont.)

	x	y	z	Patterson weights: single crystal powder	$d_{\text{Pat}^{\text{sc}}}$ $d_{\text{Pat}^{\text{p}}}$	Distances (Å)		
						d_{Riet}	d_{mrf}	d_{qsc}
C4	0.3394 (94)	-0.1979 (3)	0.1281 (8)					
	0.3447	0.2014	0.1300	7.4	0.09			
	0.3512	0.1880	0.1622	7.7	0.27	0.27	0.25	0.07
C5	0.4178 (5)	0.1670 (4)	0.3552 (9)					
						0.22	0.31	0.33
C6	0.4754 (4)	0.2247 (3)	0.5074 (12)					
	0.5000	0.2242	0.5000	8.4	0.31			
	0.5000	0.2028	0.5000	8.7	0.48	0.22	0.46	0.25
				Average:		0.30	0.24	0.21
				Maximum:		0.55	0.54	0.44

were refined and all other parameters were kept constant. To estimate the quality of the fit, a weighted R value was calculated according to:

$$wR = \left\{ \frac{\sum_{m=1}^M [1/I_{\text{obs}}(\theta_m)][I_{\text{obs}}(\theta_m) - I_{\text{calc}}(\theta_m)]^2}{\sum_{m=1}^M I_{\text{obs}}(\theta_m)} \right\}^{1/2}$$

In our case $wR = 0.148$.

Finally, the intensities were corrected for Lorentz-polarization effects, geometry factors and the reflection multiplicity, but not for absorption. This data set was used for the structure determination.

Structure determination

The crystal structure can be derived easily by direct inspection of the Patterson function in the same way as single-crystal data by obeying the following arguments: (i) the Patterson function should be dominated by the interatomic vectors from the U atom to the other atoms, since the weighting scheme shows 5% of the origin peak for a U—C distance, while the Harker vector Cl—Cl is only weighted by 2.6%; (ii) the coordination number for U should either be 6, 7 or 8 with two distances close to 1.8 Å related to the UO_2 group and further U—O distances in the range 2.2–2.6 Å; (iii) a planar alanate group $\text{C}_6\text{O}_4\text{Cl}_2$ can be expected with the hexagonal carbon ring placed into the bigger O_4Cl_2 ring; moreover, $\text{O}\cdots\text{U}$ contacts can be expected.

According to these considerations the complete structure can be recognized in the spatial arrangement for the first 25 maxima of the Patterson function calculated with the powder data (note that each maximum leads to two different positions as a result of the Patterson symmetry $I2/m$ instead of Im in the structure). Table 1* shows that the coordinates of all

atoms can be derived immediately with one exception, atom C5 within the carbon ring. This atom is also not present in the Patterson function calculated with single-crystal data. Table 1 shows for each atom (with the exception mentioned above and the exception of U) three lines: first, the line with the coordinates stemming from the final refinement of the single-crystal data; second, the coordinates derived from the Patterson function calculated with the single-crystal data [for these values in addition, the Patterson weight referring to $P(000) = 100.0$ is listed (Table 1, column 5)]; third, the coordinates derived from the Patterson function calculated with powder data, column 5 also gives the related Patterson weight for these values.

A study of Table 1 and a comparison of the different structures in Figs. 2(a) and 2(b) show that there are only small differences ($d_{\text{Pat}^{\text{sc}}}$ or $d_{\text{Pat}^{\text{p}}}$, respectively) between the two solutions compared with the final result indicated by the dots. The largest deviation from the ideal position is less than 0.5 Å (cf. Table 1, column 6).

The powder data were also successfully used for a structure determination with direct methods; since more general aspects have to be discussed in connection with this procedure the results will be given in a separate paper.

Structure refinement

In the first step of the refinement the structure model was completed. The coordinates of atom C5 were determined as the center of the triangle formed by C1, C6 and O5. The following three different types of least-squares refinement were performed. (i) A conventional Rietveld refinement was applied using the program of Bish & Howard (1988). Parameters for scaling and the profile shape, lattice parameters, anisotropic displacement parameters for U and Cl, isotropic displacement parameter for Na, and overall displacement parameter for C and O in addition to the atomic coordinates were varied in the final stage. The results are reported in Fig. 3(a) in the same way

* A list of primary diffraction data has been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71559 (10 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

as for the structure determination; the deviations (d_{Riet}) from the single-crystal structure refinement can be seen in Table 1, column 7. (ii) The Rietveld program was used for the refinement of the parameters mentioned above, apart from the atomic parameters, and also for separating the overlapping intensities to get a complete list of structure factors. The refinement was continued on the basis of this list with the single-crystal program system *ATARI CRYSTAN88* (1989) refining the scaling, the overall displacement factor and coordinates of all atoms. After this, the Rietveld process was repeated starting with the parameters of the refined model. This process was followed by another refinement with isotropic displacement parameters for the U, Cl and Na atoms in the single-crystal technique. Before the final refinement with anisotropic displacement parameters for the heavy atoms, another cycle of Rietveld refinement was applied. The final results of this mixed refinement are shown in a similar way to the complete Rietveld refinement [*cf.* Table 1, column 8 with comparative distances d_{mrf} , and Fig. 3(b)]. (iii)

After the solution of the structure, the raw data were fitted again with the procedure described above, however, this time with fixed values for FWHM. The fitting procedure was extended to all 527 expected lines, the weighting scheme for reflections in overlapping groups was taken from a structure-factor calculation based on the powder Patterson solution. This data set was refined in the single-crystal technique with the same parameter as under (ii). The result is presented in Table 1, column 9, with comparative distances d_{qsc} .

Discussion

Two different standards may be used for the discussion: (i) the well known conformation of the organic parts of the molecule, which can be regarded as an inner standard for comparison and (ii) a precise single-crystal structure determination, which could also work as a good standard. In our case there were no differences between these two standards. The

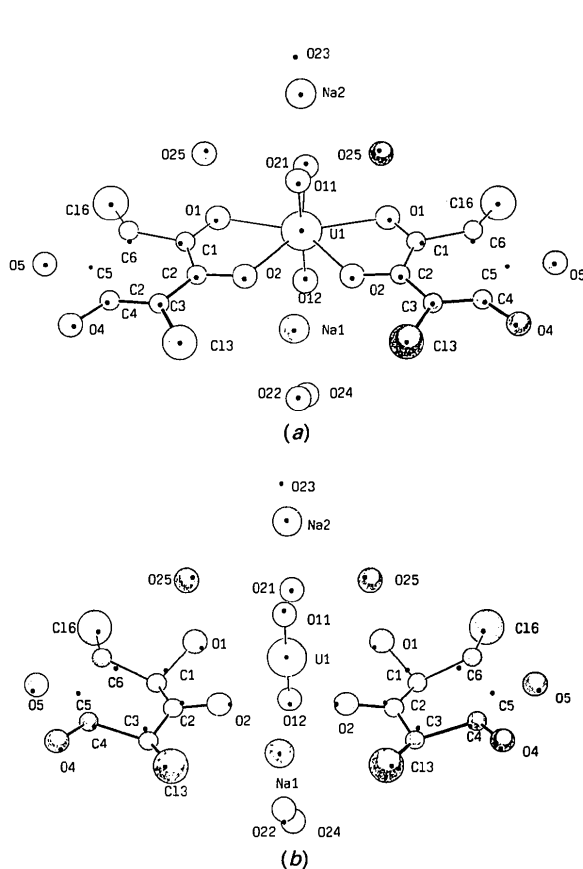


Fig. 2. (a) Structure model based on single-crystal data derived from direct Patterson function inspection (circles) compared with the refined final model (dots). (b) Structure model based on powder data derived from direct Patterson function inspection (circles) compared with the refined final model (dots).

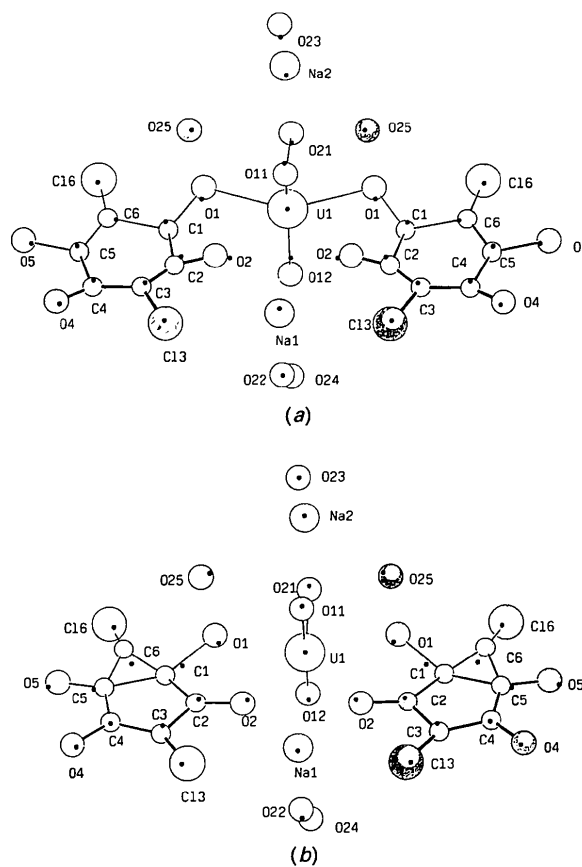


Fig. 3. (a) Structure model resulting from Rietveld refinement (circles) compared with the final structure model (dots). (b) Structure model resulting from a combined Rietveld and single-crystal refinement (circles; see text) in comparison with the final structure model (dots).

Table 2. *Information on the powder data set and refinement*

For all single-crystal techniques all 527 structure factors were used.

Measurement parameters	
Radiation	Cu $K\alpha_1$, $\lambda = 1.5405 \text{ \AA}$
Observation range	$6.0 \leq 2\theta \leq 92.0^\circ$
Step width	0.01°
Measurement time per step	3 s
Repetition factor	20
Total measurement time	6 days
No. of expected lines	527
resolved	321
overlapping	206
overlapping groups	95
Rietveld results	
No. of parameters	79
Unweighted R value	18.15
Weighted R value	15.11
R_{Bragg}	9.88

single-crystal work ($R = 0.012$; Bram, Brüderl, Burzlaff, Karayannis, Lange & Spengler, 1994) is in good agreement with the assumed conformation of the molecule, so these data are used as a reference. A comparison of the different results shows that the deviations from the correct model after refinement are of the same order as those deviations occurring directly after the structure determination. The average and maximal deviations (*cf.* Table 1, last line) give a weak indication that the application of single-

crystal refinement techniques after an adequate profile-fitting procedure might lead to better results. It is supposed that the main reason for the poor behaviour is systematic errors in the intensity measurement process and that must be investigated more carefully. On the other hand the example shows that the powder data technique can be successfully applied to crystal structure determination even in the case of a medium-sized organometallic compound.

The authors would like to thank the Internationales Büro des Forschungszentrums Jülich and the GSRT in Athens for support.

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Acta Cryst. (1994). **B50**, 50–59

Description of Coordination Geometry in Tetrahedral Metal Complexes by Symmetry-Deformation Coordinates

BY GERHARD KLEBE* AND FRANK WEBER

Main-Laboratory of BASF-AG, Carl-Bosch-Strasse, D-67056 Ludwigshafen/Rh., Germany

(Received 19 January 1993; accepted 6 September 1993)

Abstract

Coordination geometries of transition-metal complexes with Co, Ni, Cu, Pt, Pd and Rh have been analyzed by means of symmetry-deformation coordinates. These allow classification of the crystallographically observed coordination geometries with respect to reference structures of higher symmetry. Four-coordinate transition-metal complexes exhibit geometries which range from tetrahedral to square-planar. Whereas Co, Ni and Cu are found in tetra-

hedral, planar and various intermediate geometries, Pt, Pd and Rh mainly adopt planar coordination. Deformations retaining planarity show distortions from square to rectangular geometry. Complexes formed with monodentate ligands are less distorted than those containing chelate ligands. A preference for planar coordination is observed in chelated Co, Ni and Cu complexes. The data distribution indicates two alternative interconversion pathways, for the reversible transformation of a tetrahedral into a square-planar arrangement, according to angular compression- and twist-type deformations.

* Author for correspondence.