

The Crystal Structure of *o*-Phenylenediamine Dihydrochloride

BY CLAES STÅLHANDSKE

Division of Inorganic Chemistry 2, Chemical Center, The Lund Institute of Technology, P.O.B. 740, S-220 07 Lund 7, Sweden

(Received 5 February 1974; accepted 7 February 1974)

Crystals of *o*-phenylenediamine dihydrochloride, $C_6H_4(NH_2)_2 \cdot 2HCl$, are monoclinic, space group $C2/c$, with $a = 7.3352$ (2), $b = 14.5184$ (4), $c = 8.0062$ (2) Å, $\beta = 94.056$ (3)°, $Z = 4$. The structure was refined by full-matrix least-squares methods based on 695 observed reflexions to $R = 0.024$. The $C_6H_4(NH_2)_2^+$ cations are stacked in layers approximately parallel to the ab plane. The chloride ions, located between the layers, are linked *via* hydrogen bonds to the cations. Networks are thus formed, connected by van der Waals forces.

Introduction

The study of the crystal structure of *o*-phenylenediamine dihydrochloride, $C_6H_4(NH_2)_2 \cdot 2HCl$, is part of an investigation of protonated aromatic amines. The structures of $C_6H_4(NH_2)_2 \cdot HCl$ and $C_6H_4(NH_2)_2 \cdot 2HBr$ have recently been solved from X-ray data (Stålhandske, 1972*a, b*). Neutron diffraction intensities of both compounds have now been collected in order to determine the hydrogen positions and reveal the hydrogen bonding system.

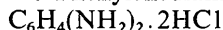
Experimental

Crystals of $C_6H_4(NH_2)_2 \cdot 2HCl$ were prepared by dissolving *o*-phenylenediamine in dilute hydrochloric acid. The crystals are transparent but become yellowish upon exposure to X-rays. The composition of the compound was checked by elementary analysis.

Weissenberg photographs showed systematic absences hkl with $h+k = 2n+1$ and $h0l$ with $l = 2n+1$, consistent with space groups $C2/c$ and Cc . The density was measured by flotation. Accurate cell dimensions were determined from a least-squares analysis of the positions of 44 reflexions measured on a diffractometer with θ -values varying between 26 and 45°.

Crystal data

o-Phenylenediamine dihydrochloride



F.W. 181.07. Monoclinic, $C2/c$ or Cc , $a = 7.3352$ (2)*, $b = 14.5184$ (4), $c = 8.0062$ (2) Å, $\beta = 94.056$ (3)°,

$V = 850.49$ Å³ at 22° C, $Z = 4$,

$D_m = 1.40$, $D_x = 1.41$ g cm⁻³; $\mu(Cu K\alpha) = 63.0$ cm⁻¹.

Intensities were collected on a computer-controlled Enraf-Nonius CAD-4 diffractometer with Cu $K\alpha$ ra-

diation and a graphite monochromator. A single crystal of dimensions $0.20 \times 0.15 \times 0.12$ mm was mounted with a along the ψ axis of the diffractometer. The ω - 2θ scan technique was used with a peak scan interval $\Delta\omega = 0.80^\circ + 0.50^\circ \cdot \tan \theta$ and background scans for $\frac{1}{4}$ of the peak scan time. A fast pre-scan was used to calculate the scan speed at which a minimum net count of 4000 was attained within a maximum measuring time of 5 min. In the range $3^\circ < \theta < 70^\circ$ 801 unique reflexions were measured of which 106 gave net intensities $I < 10$ in the pre-scan or resulted in $I < 3\sigma(I)$, where $\sigma(I)$ is based on counting statistics. The remaining 695 reflexions were corrected for Lorentz, polarization and absorption effects. The expression $p = (1 + \cos^2 2\theta_M \cos^2 2\theta) / (1 + \cos^2 2\theta_M)$ with $\theta_M = 13.3^\circ$ was used in the correction for polarization. The transmission factors, evaluated by the numerical method, varied from 0.49 to 0.58. The intensities of two standard reflexions, 354 and $48\bar{2}$, were measured after every 50 reflexions to check the stability of the crystal and the electronics. A decrease of 4% in their intensities was found during the course of the data collection. All intensities were therefore scaled with a first-order polynomial determined by least-squares.

Table 1. Atomic fractional coordinates

The values have been multiplied by 10^5 for the non-hydrogen atoms and 10^4 for the hydrogen atoms. For the numbering of the atoms, see Fig. 1.

	<i>x</i>	<i>y</i>	<i>z</i>
Cl	47676 (5)	82310 (2)	978 (4)
N	31215 (18)	66772 (8)	29286 (17)
C(1)	41084 (15)	58173 (8)	27375 (15)
C(2)	32213 (21)	49945 (9)	29778 (22)
C(3)	41133 (22)	41716 (10)	27465 (23)
H(11)	2241 (27)	6610 (10)	3577 (22)
H(12)	2650 (33)	6875 (12)	1928 (30)
H(13)	3843 (25)	7124 (12)	3399 (21)
H(2)	1982 (26)	5005 (9)	3343 (25)
H(3)	3504 (27)	3585 (17)	2944 (25)

* Numbers in parentheses represent estimated standard deviations in the least significant digits.

Table 2. *Thermal parameters*

The form of the anisotropic temperature factor is: $\exp [-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2kl\beta_{23} + 2hl\beta_{13})]$. The β values have been multiplied by 10^5 and the r.m.s. components (R_i) by 10^3 .

	β_{11}	β_{22}	β_{33}	β_{12}	β_{23}	β_{13}	R_1 (Å)	R_2 (Å)	R_3 (Å)
Cl	1030 (10)	442 (3)	1190 (9)	72 (2)	124 (2)	268 (5)	158 (1)	188 (1)	229 (1)
N	979 (22)	352 (6)	1205 (22)	51 (9)	-67 (8)	244 (18)	153 (2)	192 (2)	206 (2)
C(1)	964 (23)	309 (6)	934 (18)	18 (9)	-28 (8)	117 (16)	150 (2)	174 (2)	184 (2)
C(2)	1180 (27)	400 (7)	1600 (29)	-153 (10)	18 (9)	311 (21)	160 (2)	216 (2)	231 (2)
C(3)	2081 (36)	304 (7)	2176 (32)	-176 (12)	38 (11)	266 (27)	170 (2)	243 (2)	266 (2)

Isotropic thermal parameters (B) for the hydrogen atoms

	H(11)	H(12)	H(13)	H(2)	H(3)
B (Å ²)	3.4 (4)	5.3 (5)	3.5 (3)	3.6 (4)	5.3 (4)

Table 3. *Observed and calculated structure factors*

The columns list I , $10|F_o|$ and $10|F_c|$.

hkl	$10 F_o $	$10 F_c $	hkl	$10 F_o $	$10 F_c $	hkl	$10 F_o $	$10 F_c $
0 0 0	1000	1000	1 0 0	100	100	2 0 0	100	100
1 0 0	100	100	0 1 0	100	100	0 2 0	100	100
0 1 0	100	100	0 0 1	100	100	0 0 2	100	100
1 1 0	100	100	1 1 0	100	100	1 1 1	100	100
0 1 1	100	100	1 0 1	100	100	1 0 2	100	100
1 0 1	100	100	0 1 1	100	100	0 1 2	100	100
1 1 1	100	100	1 1 1	100	100	1 1 2	100	100
2 0 0	100	100	2 0 0	100	100	2 0 1	100	100
0 2 0	100	100	0 2 0	100	100	0 2 1	100	100
0 0 2	100	100	0 0 2	100	100	0 0 3	100	100
1 1 2	100	100	1 1 2	100	100	1 1 3	100	100
1 0 2	100	100	1 0 2	100	100	1 0 3	100	100
0 1 2	100	100	0 1 2	100	100	0 1 3	100	100
1 1 3	100	100	1 1 3	100	100	1 1 4	100	100
1 0 3	100	100	1 0 3	100	100	1 0 4	100	100
0 1 3	100	100	0 1 3	100	100	0 1 4	100	100
1 1 4	100	100	1 1 4	100	100	1 1 5	100	100
1 0 4	100	100	1 0 4	100	100	1 0 5	100	100
0 1 4	100	100	0 1 4	100	100	0 1 5	100	100
1 1 5	100	100	1 1 5	100	100	1 1 6	100	100
1 0 5	100	100	1 0 5	100	100	1 0 6	100	100
0 1 5	100	100	0 1 5	100	100	0 1 6	100	100
1 1 6	100	100	1 1 6	100	100	1 1 7	100	100
1 0 6	100	100	1 0 6	100	100	1 0 7	100	100
0 1 6	100	100	0 1 6	100	100	0 1 7	100	100
1 1 7	100	100	1 1 7	100	100	1 1 8	100	100
1 0 7	100	100	1 0 7	100	100	1 0 8	100	100
0 1 7	100	100	0 1 7	100	100	0 1 8	100	100
1 1 8	100	100	1 1 8	100	100	1 1 9	100	100
1 0 8	100	100	1 0 8	100	100	1 0 9	100	100
0 1 8	100	100	0 1 8	100	100	0 1 9	100	100
1 1 9	100	100	1 1 9	100	100	1 1 10	100	100
1 0 9	100	100	1 0 9	100	100	1 0 10	100	100
0 1 9	100	100	0 1 9	100	100	0 1 10	100	100
1 1 10	100	100	1 1 10	100	100	1 1 11	100	100
1 0 10	100	100	1 0 10	100	100	1 0 11	100	100
0 1 10	100	100	0 1 10	100	100	0 1 11	100	100
1 1 11	100	100	1 1 11	100	100	1 1 12	100	100
1 0 11	100	100	1 0 11	100	100	1 0 12	100	100
0 1 11	100	100	0 1 11	100	100	0 1 12	100	100
1 1 12	100	100	1 1 12	100	100	1 1 13	100	100
1 0 12	100	100	1 0 12	100	100	1 0 13	100	100
0 1 12	100	100	0 1 12	100	100	0 1 13	100	100
1 1 13	100	100	1 1 13	100	100	1 1 14	100	100
1 0 13	100	100	1 0 13	100	100	1 0 14	100	100
0 1 13	100	100	0 1 13	100	100	0 1 14	100	100
1 1 14	100	100	1 1 14	100	100	1 1 15	100	100
1 0 14	100	100	1 0 14	100	100	1 0 15	100	100
0 1 14	100	100	0 1 14	100	100	0 1 15	100	100
1 1 15	100	100	1 1 15	100	100	1 1 16	100	100
1 0 15	100	100	1 0 15	100	100	1 0 16	100	100
0 1 15	100	100	0 1 15	100	100	0 1 16	100	100
1 1 16	100	100	1 1 16	100	100	1 1 17	100	100
1 0 16	100	100	1 0 16	100	100	1 0 17	100	100
0 1 16	100	100	0 1 16	100	100	0 1 17	100	100
1 1 17	100	100	1 1 17	100	100	1 1 18	100	100
1 0 17	100	100	1 0 17	100	100	1 0 18	100	100
0 1 17	100	100	0 1 17	100	100	0 1 18	100	100
1 1 18	100	100	1 1 18	100	100	1 1 19	100	100
1 0 18	100	100	1 0 18	100	100	1 0 19	100	100
0 1 18	100	100	0 1 18	100	100	0 1 19	100	100
1 1 19	100	100	1 1 19	100	100	1 1 20	100	100
1 0 19	100	100	1 0 19	100	100	1 0 20	100	100
0 1 19	100	100	0 1 19	100	100	0 1 20	100	100
1 1 20	100	100	1 1 20	100	100	1 1 21	100	100
1 0 20	100	100	1 0 20	100	100	1 0 21	100	100
0 1 20	100	100	0 1 20	100	100	0 1 21	100	100
1 1 21	100	100	1 1 21	100	100	1 1 22	100	100
1 0 21	100	100	1 0 21	100	100	1 0 22	100	100
0 1 21	100	100	0 1 21	100	100	0 1 22	100	100
1 1 22	100	100	1 1 22	100	100	1 1 23	100	100
1 0 22	100	100	1 0 22	100	100	1 0 23	100	100
0 1 22	100	100	0 1 22	100	100	0 1 23	100	100
1 1 23	100	100	1 1 23	100	100	1 1 24	100	100
1 0 23	100	100	1 0 23	100	100	1 0 24	100	100
0 1 23	100	100	0 1 23	100	100	0 1 24	100	100
1 1 24	100	100	1 1 24	100	100	1 1 25	100	100
1 0 24	100	100	1 0 24	100	100	1 0 25	100	100
0 1 24	100	100	0 1 24	100	100	0 1 25	100	100
1 1 25	100	100	1 1 25	100	100	1 1 26	100	100
1 0 25	100	100	1 0 25	100	100	1 0 26	100	100
0 1 25	100	100	0 1 25	100	100	0 1 26	100	100
1 1 26	100	100	1 1 26	100	100	1 1 27	100	100
1 0 26	100	100	1 0 26	100	100	1 0 27	100	100
0 1 26	100	100	0 1 26	100	100	0 1 27	100	100
1 1 27	100	100	1 1 27	100	100	1 1 28	100	100
1 0 27	100	100	1 0 27	100	100	1 0 28	100	100
0 1 27	100	100	0 1 27	100	100	0 1 28	100	100
1 1 28	100	100	1 1 28	100	100	1 1 29	100	100
1 0 28	100	100	1 0 28	100	100	1 0 29	100	100
0 1 28	100	100	0 1 28	100	100	0 1 29	100	100
1 1 29	100	100	1 1 29	100	100	1 1 30	100	100
1 0 29	100	100	1 0 29	100	100	1 0 30	100	100
0 1 29	100	100	0 1 29	100	100	0 1 30	100	100
1 1 30	100	100	1 1 30	100	100	1 1 31	100	100
1 0 30	100	100	1 0 30	100	100	1 0 31	100	100
0 1 30	100	100	0 1 30	100	100	0 1 31	100	100
1 1 31	100	100	1 1 31	100	100	1 1 32	100	100
1 0 31	100	100	1 0 31	100	100	1 0 32	100	100
0 1 31	100	100	0 1 31	100	100	0 1 32	100	100
1 1 32	100	100	1 1 32	100	100	1 1 33	100	100
1 0 32	100	100	1 0 32	100	100	1 0 33	100	100
0 1 32	100	100	0 1 32	100	100	0 1 33	100	100
1 1 33	100	100	1 1 33	100	100	1 1 34	100	100
1 0 33	100	100	1 0 33	100	100	1 0 34	100	100
0 1 33	100	100	0 1 33	100	100	0 1 34	100	100
1 1 34	100	100	1 1 34	100	100	1 1 35	100	100
1 0 34	100	100	1 0 34	100	100	1 0 35	100	100
0 1 34	100	100	0 1 34	100	100	0 1 35	100	100
1 1 35	100	100	1 1 35	100	100	1 1 36	100	100
1 0 35	100	100	1 0 35	100	100	1 0 36	100	100
0 1 35	100	100	0 1 35	100	100	0 1 36	100	100
1 1 36	100	100	1 1 36	100	100	1 1 37	100	100
1 0 36	100	100	1 0 36	100	100	1 0 37	100	100
0 1 36	100	100	0 1 36	100	100	0 1 37	100	100
1 1 37	100	100	1 1 37	100	100	1 1 38	100	100
1 0 37	100	100	1 0 37	100	100	1 0 38	100	100
0 1 37	100	100	0 1 37	100	100	0 1 38	100	100
1 1 38	100	100	1 1 38	100	100	1 1 39	100	100
1 0 38	100	100	1 0 38	100	100	1 0 39	100	100
0 1 38	100	100	0 1 38	100	100	0 1 39	100	100
1 1 39	100	100	1 1 39	100	100	1 1 40	100	100
1 0 39	100	100	1 0 39	100	100	1 0 40	100	100
0 1 39	100	100	0 1 39	100	100	0 1 40	100	100
1 1 40	100	100	1 1 40	100	100	1 1 41	100	100
1 0 40	100	100	1 0 40	100	100	1 0 41	100	100
0 1 40	100	100						

The extinction parameter $g=0.35(3)\times 10^4$. In the last cycle of refinement the shifts in the non-hydrogen parameters were less than 0.01σ and in the hydrogen atoms less than 0.03σ . The parameters a and b used for calculating the weights were 0.0009 and 0.1 . The value of S , defined by $S=[\sum w(|F_o|-|F_c|)^2/(m-n)]^{1/2}$, where m and n are the number of observations and parameters, respectively, was 1.03 . A difference synthesis, calculated after the final least-squares refinement, showed the largest residuals in the middle of the C-C and C-N bonds. The electron densities in these peaks varied from 0.10 to 0.20 e \AA^{-3} .

The atomic scattering factors for spherically symmetric atoms were used, for the heavier atoms those suggested by Hanson, Herman, Lea & Skillman (1964), and for hydrogen that proposed by Stewart, Davidson & Simpson (1965).

The final positional parameters are given in Table 1 and the thermal parameters in Table 2. Observed and calculated structure factors are presented in Table 3. In Table 4 selected interatomic distances and angles are given. Standard deviations were calculated from the variance-covariance matrix of the final cycle of least-squares refinement.

All computations were made on the UNIVAC 1108 computer in Lund, and the programs used are listed in Table 5.

Description and discussion of the structure

The crystal structure of *o*-phenylenediamine dihydrochloride is built up of chloride ions and cations with the formula $\text{C}_6\text{H}_4(\text{NH}_3)_2^+$. The protonated molecule with the numbering of the atoms is shown in Fig. 1, and bond lengths and angles in Fig. 2. The packing of the molecules is illustrated in Fig. 3.

There are four unique carbon-carbon distances in the benzene ring as the protonated molecule in the present crystal structure has C_2 symmetry. These distances vary from $1.380(2)$ to $1.388(2)\text{ \AA}$. The weighted average $1.383(1)\text{ \AA}$ is in good agreement with the value $1.383(2)\text{ \AA}$ found in 3-aminobenzoic acid hydrochloride (Arora, Sundaralingam, Dancz, Stanford & Marsh, 1973). Two least-squares planes through the molecule

were computed, one based on all non-hydrogen atoms in the molecule and the other based only on the carbon atoms in the benzene ring (Table 6). From these calculations it is obvious that the molecule is not planar; the nitrogen atoms deviate significantly from the plane through the benzene ring. This is in contrast to the structure of *o*-phenylenediamine dihydrobromide (Stålhandske, 1972*b*), where the molecule, except for the amino hydrogens, is planar by symmetry.

The C-NH₃⁺ bond length $1.457(2)\text{ \AA}$ is shorter than both the value 1.487 \AA given by Marsh & Donohue (1967) as the average value in zwitterionic amino acids and the value 1.501 \AA found for the zwitterionic mole-

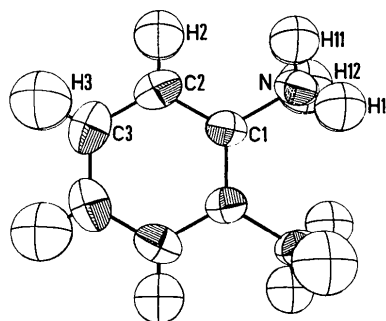


Fig. 1. The cation $\text{C}_6\text{H}_4(\text{NH}_3)_2^+$ viewed perpendicular to the ring plane. Thermal ellipsoids are drawn to enclose 75% probability.

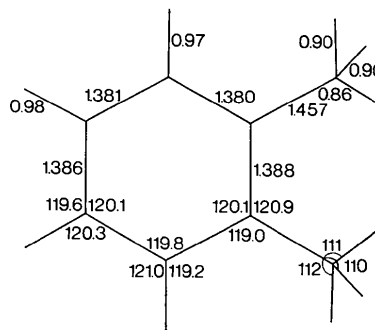


Fig. 2. Bond lengths and angles in the cation.

Table 5. Computer programs

Program	Subject	Authors
CELSIUS	Refinement of unit-cell dimensions.	J. Tegenfeldt.
DATACC	Correction for Lorentz, polarization and absorption effects and calculations of extinction components.	C. Svensson. (A modified version of <i>DATAPH</i> , written by P. Coppens, L. Leiserowitz & D. Rabinovich.)
GAASA	Symbolic addition.	O. Lindgren, O. Lindqvist & J. Nyborg.
DRF	Fourier calculations.	A. Zalkin. Modified by R. Liminga & J. O. Lundgren.
INERT	Least-squares planes.	R. Norrestam. Modified by G. Malmros.
LINUS	Full-matrix least-squares refinement with option for refinement of the extinction parameters.	W. R. Busing, K. O. Martin & H. A. Levy. Extended by P. Coppens & W. Hamilton.
WAL	Weighting-scheme analysis.	P.-G. Jönsson.
ORFFE	A crystallographic function and error program.	W. R. Busing, K. O. Martin & H. A. Levy.
ORTEP	A thermal-ellipsoid plot program.	C. K. Johnson.
SACTA	Printing of structure-factor tables.	J. Albertsson.

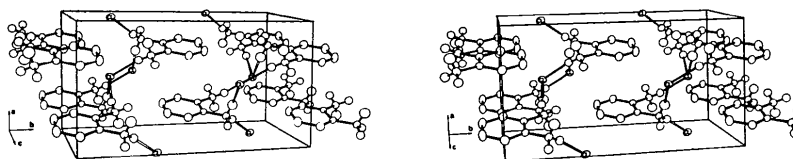


Fig. 3. Stereoscopic view of the packing in a unit cell, with covalent bonds drawn solid and hydrogen bonds open. Thermal ellipsoids are drawn to enclose 30% probability. The carbon hydrogen atoms have been excluded from the drawings.

Table 6. *Deviations from the least-squares planes through the molecule*

The lower signs refer to the superscripted atoms. The starred atoms were used to define the plane. The angle between plane I and plane II is 1° .

Plane I		Plane II	
N*, N ^{i*}	$\mp 0.034 \text{ \AA}$	N, N ⁱ	$\mp 0.059 \text{ \AA}$
C(1)*, C(1 ⁱ)*	± 0.010	C(1)*, C(1 ⁱ)*	∓ 0.002
C(2)*, C(2 ⁱ)*	± 0.022	C(2)*, C(2 ⁱ)*	∓ 0.002
C(3)*, C(3 ⁱ)*	± 0.017	C(3)*, C(3 ⁱ)*	± 0.005
H(2), H(2 ⁱ)	± 0.051	H(2), H(2 ⁱ)	± 0.031
H(3), H(3 ⁱ)	± 0.062	H(3), H(3 ⁱ)	± 0.022

cule in the structure of anthranilic acid (Brown, 1968). It is, however, in good agreement with the values found in 3-aminobenzoic acid hydrochloride 1.461(4) Å and in *o*-phenylenediamine dihydrobromide 1.445(11) Å. These short C–NH₃⁺ bonds may indicate a small amount of double-bond character in the C–N bonds.

A protonated amino group has three chloride ions as close neighbours with N...Cl distances of 3.104(1), 3.107(1) and 3.113(1) Å, and one more distant at 3.474(1) Å. The corresponding H...Cl distances are 2.21, 2.32, 2.27 and 2.96 Å. According to Hamilton & Ibers (1968) a useful criterion for hydrogen bonding is that the distance hydrogen-atom-heavy-atom should be 0.2 Å, or more shorter than the sum of the van der Waals radii. The three shorter H...Cl distances are thus hydrogen bonds, as the sum of the van der Waals radii of H and Cl⁻ is 3.0 Å. Each hydrogen atom in the NH₃⁺ group is involved in one hydrogen bond to a chloride ion.

The protonated molecules in the structure are stacked in layers approximately parallel to the *ab* plane. Along

z they are situated directly above each other but with the nitrogen ends in opposite directions. The shortest distance between these molecules is 3.76 Å.

The chloride ions, located between the layers, are each linked to three cations and *via* hydrogen bonds N–H...Cl build up networks, infinite in the *x* and *z* directions (Fig. 3). The three-dimensional structure is then formed from the networks connected by forces of van der Waals type.

The author thanks Professor Bengt Aurivillius and Dr Karin Aurivillius for many valuable discussions and comments. This investigation was supported by the Swedish Natural Science Research Council.

References

- ARORA, S. K., SUNDARALINGAM, M., DANCZ, J. S., STANFORD, R. H. & MARSH, R. E. (1973). *Acta Cryst.* **B29**, 1849–1855.
- BROWN, C. J. (1968). *Proc. Roy. Soc.* **A302**, 185–199.
- HAMILTON, W. C. & IBERS, J. A. (1968). *Hydrogen Bonding in Solids: Methods of Molecular Structure Determination*. New York: Benjamin.
- HANSON, H. P., HERMAN, F., LEA, J. D. & SKILLMAN, S. (1964). *Acta Cryst.* **17**, 1040–1044.
- MARSH, R. E. & DONOHUE, J. (1967). *Advanc. Protein Chem.* **22**, 235–256.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
- STÅLHANDSKE, C. (1972a). *Acta Chem. Scand.* **26**, 2692–2693.
- STÅLHANDSKE, C. (1972b). *Acta Chem. Scand.* **26**, 3029–3036.
- ZACHARIASEN, W. H. (1967). *Acta Cryst.* **23**, 558–564.