Acta Cryst. (1962). **15**, 11

The Crystal Structures of Pd_4Se and Pd_4S

BY FREDRIK GRØNVOLD AND ERLING RØST

Kjemisk Institutt A, Universitetet i Oslo, Blindern, Norway

(*Received* 6 *April* 1961)

The compounds Pd_4Se and Pd_4S are isostructural, space group $P\bar{4}2_1c(D_{2d}^4)$, with eight palladium atoms in general positions and two selenium (sulfur) atoms in positions $0, 0, 0; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}$. For Pd_4Se the palladium coordinates were determined to be $x=0{\cdot}374$, $y=0{\cdot}232$, $z=0{\cdot}154$, and for Pd_4S to be $x=0{\cdot}358$, $y=0{\cdot}230$, $z=0{\cdot}155$. In Pd_4Se each palladium atom is surrounded by two selenium atoms at distances of 2·46 and 2·49 Å, and ten palladium atoms at distances ranging from 2·76 to 3·12 Å. Each selenium atom is surrounded by eight palladium atoms. In Pd_4S the palladium–sulfur distances are 2·34 and 2·48 Å, and the palladium–palladium distances range from 2·78 to 3·10 Å.

Introduction

Palladium is known for its ability to form palladium-rich compounds with elements of group IV, V and VI. Among them are the compounds Pd_4Se and Pd_4S. X-ray powder photographs by Grønvold & Røst (1956) showed that the unit cells are tetragonal with the following dimensions:

$$a=5{\cdot}2324,\ c=5{\cdot}6470\ \text{Å for } Pd_4Se,$$

and

$$a=5{\cdot}1147,\ c=5{\cdot}5903\ \text{Å for } Pd_4S.$$

After annealing Pd_4Se at 450 °C. for 45 days some fairly well developed crystals were formed. Single-crystal data confirmed the absence of reflections hhl when l is odd, and $h00$ when h is odd. The probable space group is thus $P\bar{4}2_1c$ (D_{2d}^4).

On the basis of density measurements it was concluded that the unit cells contain 8 Pd atoms and 2 Se, or 2 S atoms, respectively.

Determination of the structure

In the space group $P\bar{4}2_1c$ the palladium atoms must be accommodated in the eightfold general positions and the selenium (sulfur) atoms in the twofold positions as follows:

$$\begin{array}{lll} 8\,\text{Pd in } (e) & x, y, z; & \tfrac{1}{2}-x, \tfrac{1}{2}+y, \tfrac{1}{2}-z; \\ & \bar{x}, \bar{y}, z; & \tfrac{1}{2}+x, \tfrac{1}{2}-y, \tfrac{1}{2}-z; \\ & \bar{y}, x, \bar{z}; & \tfrac{1}{2}+y, \tfrac{1}{2}+x, \tfrac{1}{2}+z; \\ & y, \bar{x}, \bar{z}; & \tfrac{1}{2}-y, \tfrac{1}{2}-x, \tfrac{1}{2}+z; \\ 2\,\text{Se(S) in } (a) & 0, 0, 0; & \tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2}. \end{array}$$

Approximate x, y and z parameters for the palladium atoms were found by trial and error on comparing the calculated intensities with those observed from powder photographs of Pd_4Se and Pd_4S. These values were arrived at:

$$x=0{\cdot}37,\ y=0{\cdot}23,\ z=0{\cdot}155 \text{ for } Pd_4Se$$

and

$$x=0{\cdot}358,\ y=0{\cdot}230,\ z=0{\cdot}155 \text{ for } Pd_4S\,.$$

The observed intensities for Pd_4S, as well as those calculated using the above parameters, are listed in Table 1.

For Pd_4Se the structure could be refined by means of Fourier methods. Weissenberg photographs were taken in the $h0l$ zone of Pd_4Se using copper radiation. The crystal used had a cross-section of about 0·10 × 0·12 mm. Relative intensities were estimated visually, using the double film technique. Out of 37 possible reflections, 33 could actually be observed. The intensities were corrected for Lorentz and polarization factors and for absorption ($\mu R=11$).

Table 1. *Observed and calculated intensities for* Pd_4S

hkl	I_o	I_c	*hkl*	I_o	I_c	*hkl*	I_o	I_c
101	3	3·2	310	5	4·0	303	—	1·0
110	—	0·0	311	14	12·5	401	21	14·6
002	8	8·0	222	4	3·1	410	6	4·2
200	35	39	203	—	0·3	204	9	6·7
102	30	31	302	20	14·2	313	23	17·1
201	16	21	213	6	4·5	411	—	0·7
210	70	71	320	10	6·9	330	—	0·8
112	100	100	312	8	1·1	214	15	11
211	50	51	004		4·5	402	—	0·0
202	12	9·6	321	20	15	420	5	3·8
220	5	3·8	104	3	2·5	412	4	2·7
212	25	24	114	15	12·2	323	14	9·3
103	10	8·9	400	—	0·1	421	12	7·5
301	5	3·6	322	20	12·2			

Table 2. *Observed and calculated structure factors for* Pd_4Se

$h0l$	$\|F_o\|$	F_c	$h0l$	$\|F_o\|$	F_c	$h0l$	$\|F_o\|$	F_c
200	97	+88	201	106	+109	401	122	+135
400	25	+22	202	72	+84	402	37	−32
600	15	+21	203	20	−25	403	31	−33
002	85	+52	204	82	−91	404	32	+28
004	105	−107	205	62	−67	405	85	−102
006	112	−126	206	36	−31	501	67	−72
101	—	−4	301	70	+62	502	—	+9
102	96	−104	302	93	−97	503	50	−50
103	102	+104	303	—	+3	504	—	+6
104	62	−50	304	52	−52	601	45	+37
105	24	−21	305	33	+24	602	32	+32
106	26	+22	306	25	+25	603	12	−9
107	8	−9						

The Fourier synthesis was based upon the plane group *pmg*, with the origin placed at a center of symmetry $(\frac{\bar{1}}{4}, \frac{\bar{1}}{4})$. In this plane group the positions of the eight palladium atoms are given by two fourfold positions x, z; $\bar{x}, \bar{z}$; $\frac{1}{2}+x, \bar{z}$; $\frac{1}{2}-x, z$, and the positions of the two selenium atoms given by the twofold positions $\frac{1}{4}, z$; $\frac{3}{4}, \bar{z}$. The plane group *pmg* does not possess symmetry as high as the $h0l$ projection of the space group $P\bar{4}2_1c$. The z parameter of the twofold positions should in fact be exactly $\frac{1}{4}$. The second Fourier synthesis gave the following parameters in the plane group:

$$x_1 = 0{\cdot}624,\ z_1 = 0{\cdot}404$$
$$x_2 = 0{\cdot}018,\ z_2 = 0{\cdot}096\ .$$

The projection along the b-axis of Pd_4Se is shown in Fig. 1.

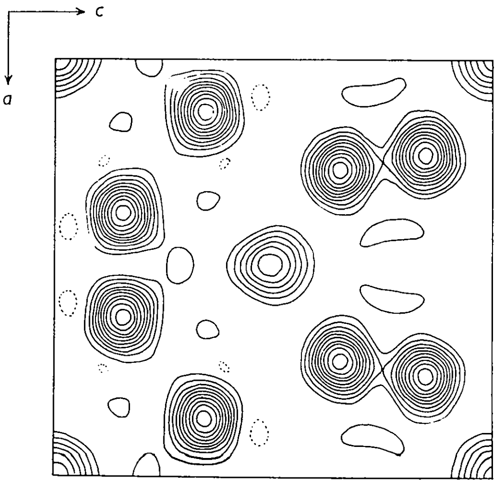

Fig. 1. Fourier projection of Pd_4Se on (010). Contours are at intervals of 10 e.Å^{-2}. The zero contours are not shown. The −10 e.Å^{-2} contours are broken.

Structure factors were calculated for this arrangement and adjusted using a temperature factor ($\exp[-B \sin^2 \theta/\lambda^2]$ with $B = 1{\cdot}3$ Å^2). F_c and F_o were put on the same scale by making their sums equal. The observed and calculated structure factors are listed in Table 2. The value of the reliability index $R = \Sigma \| |F_o| - |F_c| \| / |F_o|$ is 0·11.

From the electron-density projection the following parameters are obtained in the space group $P\bar{4}2_1c$:

$$x = 0{\cdot}374,\ y = 0{\cdot}232,\ z = 0{\cdot}154\ .$$

These values do not differ much from those found by the powder method, but are considered more accurate.

A projection of the Pd_4Se structure along the c-axis is shown in Fig. 2. Each palladium atom is coordinated by two selenium atoms at distances of 2·46 and 2·49 Å, and ten palladium atoms at the following distances: 2·76, 2·80(2), 2·84(2), 2·93(2), 3·10 and 3·12(2) Å. The selenium atoms have a body-centered arrangement and each selenium atom is surrounded by eight palladium atoms at distances of 2·46(4) and 2·49(4) Å.

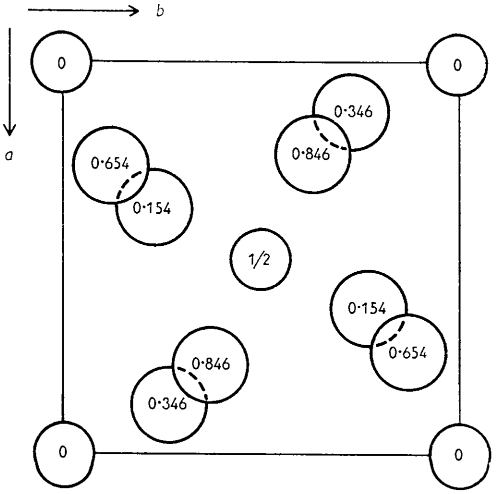

Fig. 2. The structure of Pd_4Se viewed along the c-axis. Large circles indicate the palladium atoms and small circles the selenium atoms. Figures in the circles give the z-parameters of the atoms.

In the Pd_4S structure the atomic arrangement is analogous. The palladium–sulfur distances are 2·34 and 2·48 Å, and the distances between the palladium atoms are: 2·78, 2·78(2), 2·80(2), 2·86(2), 2·98(2) and 3·10 Å.

The bonds in the compounds, especially those between the palladium atoms, are considered to be chiefly of metallic character. This is apparent from the palladium–palladium distances, which are only slightly larger than the distance 2·7505 Å in metallic palladium according to the data by Swanson & Tatge (1953). The varying bond distances between the palladium atoms are probably a compensation for the lack of coordination symmetry.

The authors express their appreciation to Prof. Haakon Haraldsen for his interest in this study and for making laboratory facilities avaiable.

References

GRØNVOLD, F. & RØST, E. (1956). *Acta Chem. Scand.* **10**, 1620.

SWANSON, H. E. & TATGE, E. (1953). *U. S. Nat. Bur. Stand.*, Circular 539, Vol. 1, p. 21.

Acta Cryst. (1962). **15**, 13

Phasenbestimmung durch Quadrierung der Elektronendichte im Bereich von 2 Å- bis 1,5 Å-Auflösung

VON WALTER HOPPE

Abteilung für Röntgenstrukturforschung am Max-Planck-Institut für Eiweiss- und Lederforschung, München, und Abteilung für Strukturforschung am Physikalisch-Chemischen Institut der Technischen Hochschule München, Deutschland

(*Eingegangen am* 26. *Januar* 1961)

An approximate method for the phase determination of additional structure factors, necessary for increasing the resolving power of the electron-density projection from 2 to 1·5 Å, is described. This method, which is of special interest for phase determination of protein crystals, is based on the similarity between the squared 2 Å projection and the 1·5 Å electron-density map of structures containing light elements only. The method is applied to some examples.

Einleitung

Die für die Strukturuntersuchung von Protein-Einkristallen bisher ausschliesslich verwendete Methode des multiplen isomorphen Ersatzes erfordert die Paralleluntersuchung einer grösseren Anzahl von isomorphen Schweratomderivaten des Proteins. So mussten z. B. im Falle der Strukturuntersuchung von Myoglobin insgesamt 6 verschiedene Kristallsorten gleichzeitig untersucht werden (Bodo *et al.*, 1959). Die damit verbundene Vervielfachung der experimentellen Arbeitszeit ist bei den grossperiodigen Proteingittern derart beträchtlich, dass bisher die Strukturanalyse nur bis zu einer willkürlichen Auflösungsgrenze von 2 Å (im Falle von Myoglobin) (Kendrew *et al.*, 1960) vorangetrieben werden konnte. Die Anwendung der Methode des multiplen isomorphen Ersatzes wird ferner durch eventuelle kleine Abweichungen der Isomorphie der einzelnen Derivate beeinträchtigt; solche Phasenfehler wirken sich wiederum bei hohen Auflösungen besonders aus.

Eine Auflösung von 2 Å gestattet bereits ein weitgehendes Erkennen der atomaren Struktur, wenn die entsprechenden Fouriersynthesen mit Kenntnis der bekannten Atomabstände, Bindungswinkel und anderer stereochemischer Daten interpretiert werden. Es erscheint daher möglich, ein Modell auf Grund der Ergebnisse der 2 Å-Auflösung zu konstruieren und die aud diesem Modell berechneten Phasen von Strukturfaktoren zur Phasierung der experimentell gemessenen Strukturfaktoren einer Auflösung von 1,5 Å zu verwenden.*

In der vorliegenden Arbeit wird nun ein neues Verfahren für eine Näherungsbestimmung dieser Restphasen vorgeschlagen. Es beruht auf gewissen allgemeinen strukturellen Zügen der Elektronendichtefunktion in bestimmten Auflösungen und liefert eine Elektronendichte-Projektion mit einer Auflösung von 1,5 Å ohne modellmässige Vorstellungen. Diese Elektronendichte-Projektion kann zur Aufstellung eines Modelles benutzt werden, das dann selbstverständlich über wechselseitige Berechnungen von Elektronendichte-Projektionen und Modellstrukturfaktoren weiter verfeinert werden kann. Da dieses Modell auf einer — wenn auch noch mit Phasenfehlern versehenen — Elektronendichte-Projektion höherer Auflösung (1,5 Å) beruht, (die naturgemäss zusätzliche experimentelle Informationen enthält) so sollte das Aufstellen des ersten Modells mit grösserer Sicherheit als aus der 2 Å-Elektronendichte-Projektion möglich sein. Voraussetzung ist natürlich, dass der Phasenbestimmungsprozess nicht derartige Fehler einführt, dass die zusätzlichen Fourierkoeffizienten das ursprüngliche 2 Å-Bild verschlechtern. Zur Beurteilung der Güte der Phasenbestimmung wurden daher im Laufe dieser Arbeit Testbeispiele durchgerechnet.

---

* Dies ist die experimentell ungefähr erreichbare Grenzauflösung bei Proteinkristallen.