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SYNTHESIS AND STRUCTURE OF $BaPdS_2$

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Summary

$BaPdS_2$ crystallizes in the space group *Cmcm* with $a = 6.783(1)$ Å, $b = 10.634(2)$ Å, $c = 5.627(1)$ Å, $Z = 4$. The crystal structure was determined from single crystal diffractometer data. $BaPdS_2$ is isotypic with $BaNiO_2$ containing infinite zigzag chains, ${}^1_\infty[PdS_{4/2}]^{2-}$, in which the palladium atoms are planar coordinated by the sulphur ligands.

In this context the relationship to the K_2PdAs_2-structure type with analogous zigzag chains, ${}^1_\infty[Pd(As_2)_{2/2}]^{2-}$, as well as recently published calculations dealing with this zigzag chain and the linear arrangement found in the K_2PtS_2 structure will be discussed.

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1. Introduction

In ternary compounds of the stoichiometry A_xMX_2, where A is an alkali metal ion, M is a transition metal atom with d^8 configuration and X is oxygen or sulphur, a characteristic framework structure has been found. In it the M atoms are always coordinated by a planar arrangement of X atoms, the resulting rectangular arrays being linked one-dimensionally by their sides forming infinite linear chains ${}^1_\infty[MX_{4/2}]^{x-}$. Examples are the oxides $ACuO_2$, $AAuO_2$ ($A \equiv$ K, Rb or Cs) [1, 2] and K_2PdO_2 [3] as well as the sulphides A_2PtS_2 ($A \equiv$ Na, K or Rb) [4, 5] and Na_2PdS_2 [4]. However, a structure determination of the ternary alkaline-earth metal oxide $BaNiO_2$ from powder data leads to a framework with a zigzag chain of once more one-dimensionally linked planar arrangements of X atoms [6, 7]. The new compound $BaPdS_2$ crystallizes in the same structure type. The synthesis, the structure determination and a discussion of the two different chain structures are the subject of this paper.

2. Preparation and characterization

All attempts to produce a barium thiopalladate through a reaction of a mixture of $BaCO_3$ and palladium powder in a stream of dry H_2S have resulted

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in a mixture of BaS and PdS. However, the use of $BaPd(CN)_4 \cdot 4H_2O$ [8] as a starting material, which was heated for 3 h at 870 K in a stream of dry H_2S, yielded $BaPdS_2$ as a black powder with a bluish lustre. Black rectangular prismatic crystals with the same bluish metallic lustre resulted from the reaction of larger $BaPd(CN)_4 \cdot 4H_2O$ crystals with sulphur in a slow, dry and oxygen-free argon stream (3 h at 870 K).

For analysis the compound was dissolved in aqua regia and evaporated with HCl several times whereby $BaSO_4$ partially precipitated. The acidic solution was then diluted with H_2O. Then $BaSO_4$ was completely precipitated by the addition of H_2SO_4. The precipitate was weighed (found: 44.45% Ba, calculated: 44.61% Ba). The palladium in the filtrate was reduced by formic acid to its elemental form in a weakly acidic solution. The palladium was weighed (found: 34.72% Pd, calculated 34.56% Pd). The sulphur was determined as the difference (remainder: 20.72% S, calculated: 20.83% S).

3. Structure determination

Weissenberg and precession patterns from a single crystal (0.05 mm × 0.025 mm × 0.15 mm) showed orthorhombic symmetry. The lattice constants $a = 6.783(1)$ Å, $b = 10.634(2)$ Å, $c = 5.627(1)$ Å were determined by a least-squares refinement of Guinier–Simon data (α-quartz standard). According to the volume increment considerations of Biltz [9] the unit cell contains four formula units of $BaPdS_2$. The systematic absences, hkl: $h + k \neq 2n$, $h0l$: $l \neq 2n$ lead to the possible space groups *Cmcm*, *C2cm* and *Cmc*2.

The intensities of one octant of the reflection sphere were measured with a four-circle diffractometer (CAD 4, Enraf-Nonius, Delft, Ag Kα radiation, graphite monochromator, $1° \leqslant \theta \leqslant 24°$, ω–2θ scan). The lattice constants given above were verified within the threefold standard deviations using 23 reflections chosen at random. In total 1045 symmetrically inequivalent reflections were measured, from which 755 with $F_o^2 \geqslant 3\sigma(F_o^2)$ were used. The structure amplitudes were weighted with the factors $1/\sigma(F_o^2)$ where the standard deviations were based on the intensities. All calculations were carried out on a PDP 11/45 computer with the program system SDP [10]. The structure was refined in the space group with the highest symmetry, *Cmcm*.

According to the Patterson synthesis the palladium atoms occupy the positions 4a and the barium atoms the positions 4c with $y \approx 0.34$. After a few cycles of least-squares refinement the sulphur position could be determined by a difference Fourier synthesis. Accordingly the sulphur atoms occupy the positions 8g with $x \approx 0.25$ and $y \approx 0.08$. A least-squares refinement of the atom positions converged immediately with the previously described structure proposal. Without absorption and extinction corrections and with isotropic temperature factors an R value of 0.075 ($R_w = 0.051$) was obtained. With anisotropic temperature factors the R value dropped to 0.042 ($R_w = 0.045$).

TABLE 1

Positional and thermal parameters for $BaPdS_2$

	x	y	z	U_{11} ($\times 10^2$ Å^2)	U_{22} ($\times 10^2$ Å^2)	U_{33} ($\times 10^2$ Å^2)	U_{12} ($\times 10^2$ Å^2)	U_{13} ($\times 10^2$ Å^2)	U_{23} ($\times 10^2$ Å^2)
Pd 4a	0.0	0.0	0.0	0.88(2)	1.23(2)	1.00(2)	0	0	−0.10(2)
Ba 4c	0.0	0.34915(4)	1/4	1.38(2)	0.91(1)	2.01(2)	0	0	0
S 8g	0.2367(2)	0.0958(1)	1/4	1.01(4)	1.28(4)	1.44(4)	0.01(4)	0	0

Space group, *Cmcm*; $a = 6.783(1)$ Å, $b = 10.634(2)$ Å, $c = 5.627(1)$ Å, $Z = 4$; extinction coefficient, 1.98×10^{-6}.
The anisotropic temperature factors are given by the expression $\exp\{-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + \ldots + 2U_{23}klb^*c^*)\}$.
The estimated standard deviations are given in parentheses.

After introduction of the extinction correction the refinement converged to an R value of 0.025 ($R_w = 0.023$) (extinction coefficient, 1.98×10^{-6}). After the last refinement the difference Fourier synthesis showed a residual electron density of less than 1 electron $Å^{-3}$. The position and temperature parameters are shown in Table 1. F_o and F_c values will be provided by the authors on request.

4. Structure description and discussion

Figure 1 shows the *bc* projection and Fig. 2 a perspective view of the crystal structure of $BaPdS_2$. Interatomic distances and selected bond angles are given in Table 2. $BaPdS_2$ crystallizes in the $BaNiO_2$ structure type [6, 7]. As expected from the d^8 configuration the palladium atoms are in a strict planar coordination formed by four sulphur atoms. These planar units are linked by opposite sides and form a zigzag chain, $^{1}_{\infty}[PdS_{4/2}]^{2-}$, along the [001] direction. Along this direction the crystals easily form fibres under mechanical stress. The angle between the square-planar units in the zigzag chain is 108.18(6)°. This bonding leads to relatively short palladium distances of 2.814(1) Å, which are only 2.3% larger than those in palladium metal (2.7505 Å).

As shown in Fig. 3, the barium atoms have eight nearest sulphur neighbours. The coordination polyhedron is an irregular eight-sided polyhedron with C_{2v} symmetry. Its two rectangular and two trapezoidal faces are perpendicular to (100), two of its isosceles triangular faces run parallel with (100) while the remaining isosceles triangular faces are slightly inclined to (100) so that the angle of intersection of these pairs of triangular faces is 176.85(5)°. In the [100] direction the sulphur polyhedron of the barium

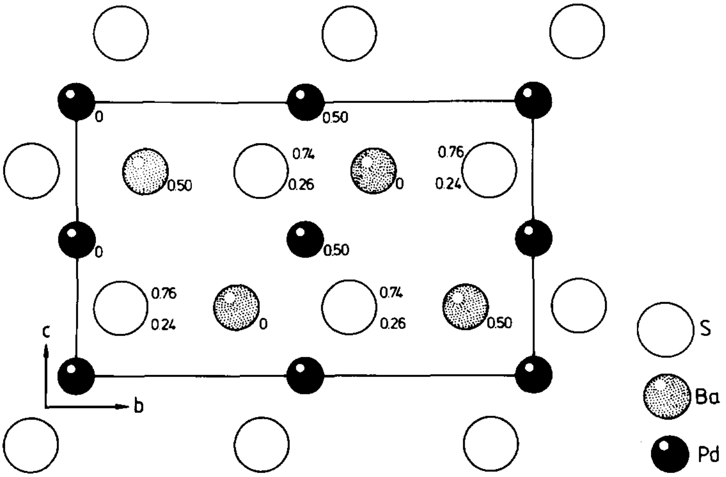

Fig. 1. Structure of $BaPdS_2$, projection along [100].

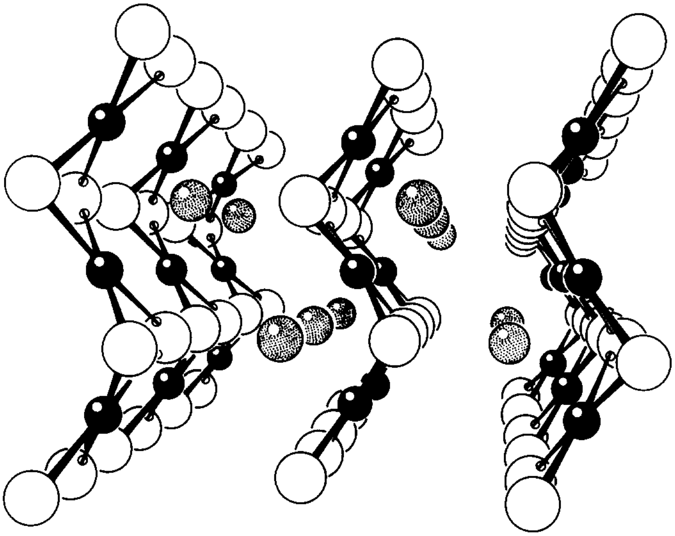

Fig. 2. Perspective view of the structure of $BaPdS_2$ along [100]. The symbols correspond to those of Fig. 1.

TABLE 2

Selected interatomic distances (in ångströms) and angles for $BaPdS_2$

Pd–Pd	2.814(1) 2×	S–S	3.572(3) 3×
Pd–S	2.365(1) 4×	around Ba	3.211(3) 1×
Pd–Ba	3.970(1) 2×		3.474(1) 4×
Pd–Ba	4.007(1) 4×		4.325(2) 4×
			5.627(1) 2×
Ba–S	3.136(1) 2×		
	3.173(1) 2×	Angles in the Pd–S rectangle	
	3.384(1) 4×		85.50(5)° 2×
			94.50(5)° 2×
S–S	3.211(3) 2×		
around Pd	3.474(1) 2×	Angle in between the Pd-centroid	
		Pd–S rectangles	108.18(6)°
Ba–Ba	4.267(1) 2×		
	4.885(1) 4×		

The estimated standard deviations are given in parentheses.

atom joins, with its convex intersection of triangular faces, an empty sulphur polyhedron, which is concave at this intersection. The empty polyhedron, too, has C_{2v} symmetry. Its two rectangular faces are centred by the palladium atoms. The two joined polyhedra form a distance along [100] equal to the *a* axis parameter, and fill the space completely.

Other compounds which also show zigzag chains of planar ligand coordination spheres centred by transition metal atoms are the ternary pnictides K_2PdAs_2 [11], K_2PdP_2 and K_2PtAs_2 [12], isotypic with each other. Here

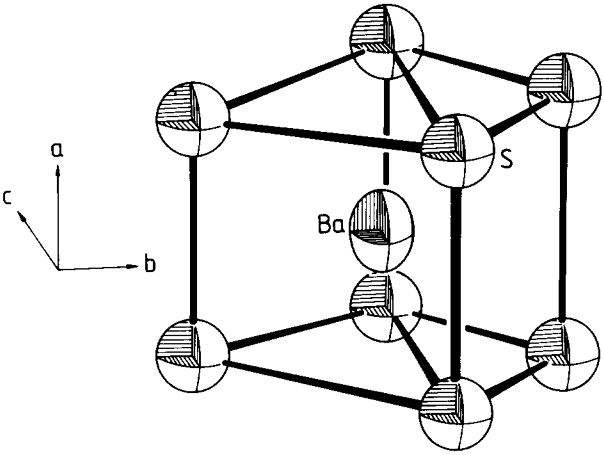

Fig. 3. The sulphur coordination sphere of the barium atoms.

the planar coordination differs in that two pnictide dumbbells coordinate the metal atoms with d^8 configuration yielding the connection formula $^1_\infty[Pd(As_2)_{2/2}]^{2-}$. These compounds again crystallize in the space group *Cmcm* with $Z = 4$. They may be described as a filled $BaNiO_2$-structure type, where the transition metal, the pnicogen and K(1) occupy the same atomic positions with nearly the same atomic parameters as found in $BaPdS_2$. However, the coordination number for K(1) is reduced to six. The coordination polyhedron is here a trigonal prism in which the triangular faces are parallel with (100), recognizable as a fragment of the polyhedron around the barium atom shown in Fig. 3. K(2) occupies the empty void in the $BaNiO_2$-structure type. Two of the edges parallel to [100] are formed by pnictide dumbbells, while the third edge parallel with [100] is a non-bonding pnicogen–pnicogen distance. In this strongly distorted trigonal prism K(2) has two short distances to the transition metal atoms.

Recently published band structure calculations [13] show in accordance with experimental results that a zigzag chain should be stable in the case of the compound K_2PdAs_2 where dumbbells of non-metal atoms occur; with isolated non-metal ligands the planar linear chain (K_2PtS_2 type) should be energetically more favourable. Additional calculations [14] indicate that only about 0.38 eV per formula unit are necessary to transform the linear chain into the zigzag geometry observed in $BaPdS_2$. All calculations mentioned above are based on the model of isolated chains, thus neglecting the complete atomic arrangement of the crystal structure of the ternary compounds. Therefore the transition of the linear chain in the compound K_2PdS_2 [15] into the zigzag chain in $BaPdS_2$ can only be induced by a change in stoichiometry and charge. Primary calculations of the electrostatic part of the lattice energies suggest that a zigzag chain is more favourable for the stoichiometry $APdS_2$, whereas a linear chain is more favourable for the stoichiometry A_2PdS_2.

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