ELSEVIER

Journal of Alloys and Compounds 224 (1995) 190–193

Journal of
ALLOYS
AND COMPOUNDS

Synthesis and crystal structure of $BaPd_2S_4$ – a sulphide–disulphide compound, $BaPd_2S_2(S_2)$*

J. Huster, W. Bronger

Institut für Anorganische Chemie der Technischen Hochschule Aachen, Prof.-Pirlet-Str. 1, D-52056 Aachen, Germany

Received 15 December 1994

Abstract

Single crystals of $BaPd_2S_4$ have been grown in an H_2S-stream from a mixture of $BaPd(CN)_4 \cdot 4H_2O$ and BaS in a KSCN-melt. The crystal structure was solved using single crystal X-ray diffraction methods. $BaPd_2S_4$ is monoclinic, $P2_1/m$, $a = 7.252(1)$ Å, $b = 6.764(1)$ Å, $c = 6.687(1)$ Å, $\beta = 110.45(1)°$, $Z = 2$. The new structure type contains sulphur–palladium–sulphur layers in which two crystallographic-different palladium (II) ions are planar coordinated by sulphide and disulphide ions. The layers are connected by barium ions.

Keywords: Synthesis; Crystal structure; Sulphide–disulphide compound; Single crystal X-ray diffraction

1. Introduction

The ternary barium compounds $BaNiS_2$ [1], $BaPdS_2$ [2] and $BaPt_2S_3$ [3] and their structures have been known for a long time.

In $BaNiS_2$ the basic structural unit consists of a nickel atom which is coordinated to five sulphur atoms at the apices of an almost regular square pyramid. Each square-pyramidal unit shares its equatorial edges with four inverted units, thus building up two-dimensional layers, $^2_\infty[NiSS_{4/4}{}^{2-}]$.

In $BaPdS_2$ and $BaPt_2S_3$ the basic structural unit is a square plane of sulphur atoms centred by the transition metal. In both structures the planar units are linked by their sides forming infinite chains. In the case of $BaPdS_2$ these $^1_\infty[PdS_{4/2}{}^{2-}]$-chains are isolated and adopt a zigzag configuration. In the structure of $BaPt_2S_3$, however, infinite linear chains build up a three dimensional linkage, forming the polyanion $^3_\infty[PtS_{2/4}\text{-}S_{2/2}{}^{1-}]$.

As the formula implies, in every square plane of sulphur atoms two sulphur atoms are fourfold coordinated by platinum. This coordination is tetrahedral as is the situation for every sulphur in the PtS-type structure, $^3_\infty[PtS_{4/4}]$ [4]. Since these two sulphur atoms are trans to one another in the square, they are thus members of two different chains which run perpendicular to the considered chain.

2. Experimental

A melt of KSCN in an alumina boat containing as starting materials $BaPd(CN)_4 \cdot 4H_2O$ [5] and BaS was heated for 18 h at 730 K in a stream of dry H_2S. The solidified melt was dissolved with water. The remaining bluish black needle-shaped crystals were washed with water and ethanol, and after drying in vacuum, stored under argon.

Single crystals were isolated and Weissenberg- and Precession patterns showed monoclinic symmetry where the *b* direction is the needle axis. The systematic absence $0k0: k \neq 2n$ leads to the possible space groups $P2_1/m$ or $P2_1$.

Intensity data of a single crystal were collected on a four-circle diffractometer (CAD4, Enraf–Nonius, Delft) using the -2Θ scan mode. The lattice constants at 295 and 8 K are based upon a powder diffraction measurement using an Huber–Guinier apparatus. The crystal structure was solved by direct methods and refined in the space group $P2_1/m$ using the NRC-VAX program [6]. Details of the single crystal and the powder data collection are summarized in Table 1, whilst the

---

* Dedicated to Professor P. Paetzold on the occasion of his 60th birthday.

SSDI 0925-8388(95)01541-8

Table 1
Crystal data and structure refinement for $BaPd_2S_4$

Diffractometer type	Enraf-Nonius, CAD-4	
Monochromator	Graphite	
Temperature	293(2) K	
Wavelength	AgK_α	
Crystal system	Monoclinic	
Space group	$P2_1/m$ (No. 11)	
Unit cell dimensions based on HUBER-Guinier data $CuK_{\alpha 1}$ Si as intern standard		
	293 K	8 K
	$a = 7.252(1)$ Å	$a = 7.2399(6)$ Å
	$b = 6.764(1)$ Å	$b = 6.7509(5)$ Å
	$c = 6.687(1)$ Å	$c = 6.6664(6)$ Å
	$\beta = 110.45(1)°$	$\beta = 110.40(1)°$
	97 observed values	110 observed values
	118 *hkl*-values	134 *hkl*-values
Crystal size	0.02 mm × 0.35 mm × 0.01 mm	
2θ range for data collection	1–48°	
Index ranges	$h \pm 10$, $k \pm 9$, $l \pm 9$	
Reflections collected	3875	
Unique reflections	1051	
Reflections with $I > 3\sigma(I)$	757	
Parameters	41	
Final R values	$R = 0.023$, $R_w = 0.030$ ($w = 1$)	
Extinction coefficient	0.031(2)	
Final Δ-Fourier-map, deepest hole, highest peak	-1.33 e Å^{-3}, 1.72 e Å^{-3}	

final atomic parameters, anisotropic thermal parameters, and selected bond lengths and angles are given in Tables 2–4.

3. Structure description and discussion

Fig. 1 shows the *ac*-projection of the crystal structure which illustrates that the structure can be described in terms of a layer structure. The palladium atoms lie, apart from a slight deviation of Pd2, in the *bc*-plane. The sulphur atoms S1 and S2 coordinate the palladium atoms and form slightly distorted planes on both sides of the palladium plane. Consequently, sulphur–palladium–sulphur layers arise parallel to the *bc*-plane. They are connected by the barium ions which also include the sulphur atoms S3 in their coordination sphere. Fig. 2 shows a perspective view of one sulphur–palladium–sulphur layer. The sulphur atoms S3 are omitted for clarity and the planar sulphur coordination around the palladium ions is represented simply by squares. One can distinguish two kinds of chains along the [010]-direction. Both chains contain square planes of sulphur atoms centred with palladium. In the linear chain, centred by Pd2, the square planar sulphur units, formed by S1, are connected on opposite sides. This pattern is known from the K_2PtS_2-type structure [7] as an isolated chain, $^{1}_{\infty}[\mathrm{PtS}_{4/2}{}^{2-}]$. In the other chain, centred by Pd1, the square planar sulphur units, formed by S1 and S2, are connected via S2 corners which lie diagonally opposite in the square. This type of linkage has been observed, in the $SrPdO_3$-type structure [8] as an isolated and linear chain, $^{1}_{\infty}[\mathrm{PdO_2O_{2/2}}{}^{4-}]$. Since in the structure under discussion, both types of chains are connected via the common sulphur atoms S1 to one plane, the chains are forced to keep abreast of one another. To attain this, the corner-connected chains tilt their square plane units alternatively out of the plane in a concertina-type fashion. The planes form an angle of 92.8(1)° to each other. The connecting sulphur atoms S2 in this chain constitute one end of a sulphur-dumbbell which is completed by S3. These dumbbells can be described as end-on bonded via S2 with respect to the square plane units around Pd1 and project in this way alter-

Table 2
$BaPd_2S_4$, atomic parameters x, y, z and B_{iso} (Å^2), e.s.ds. refer to the last digit

		x	y	z	B_{iso}
Pd1	2a	0	0	0	0.65(3)
Pd2	2e	0.9877(1)	3/4	0.4810(1)	0.62(3)
Ba	2e	0.4918(1)	1/4	0.2818(1)	0.96(2)
S1	4f	0.1481(2)	0.4953(3)	0.3704(3)	0.72(6)
S2	2e	0.7886(4)	1/4	0.0290(4)	0.75(8)
S3	2e	0.4928(4)	3/4	0.2055(4)	1.08(9)

Table 3
$BaPd_2S_4$, anisotropic displacement parameters $U(i,j)$ [$Å^2 \times 100$], e.s.ds. refer to the last digit

	U11	U22	U33	U12	U13	U23
Pd1	0.92(3)	0.71(3)	0.77(3)	0.05(3)	0.21(2)	−0.02(3)
Pd2	1.13(3)	0.52(3)	0.76(3)	0.0	0.36(3)	0.0
Ba	1.16(3)	1.25(3)	1.31(3)	0.0	0.51(2)	0.0
S1	1.11(7)	0.77(7)	0.81(6)	0.01(6)	0.29(5)	0.02(6)
S2	0.86(10)	1.01(11)	0.89(9)	0.0	0.19(8)	0.0
S3	1.28(11)	1.54(11)	1.07(10)	0.0	0.15(9)	0.0

Table 4
$BaPd_2S_4$, selected distances (Å) and angles (°)

Pd1–Pd1	3.3820(5)	Pd1–S1	2.331(2) 2×
Pd2–Pd2	3.3916(5)	–S2	2.336(2) 2×
Pd1–Pd2	3.6624(9)		
Pd2–Pd2–Pd2	171.38(5)	Pd2–S1	2.322(2) 2×
		–S1	2.338(2) 2×
S2–S3	2.093(3)		
Pd2 is 0.126(1) Å out of plane formed by S1			
Ba–S2	3.168(3)	Ba–S3	3.296(3)
–S1	3.217(2) 2×	–S3	3.394(3)
–S1	3.310(2) 2×	–S3	3.421(1) 2×

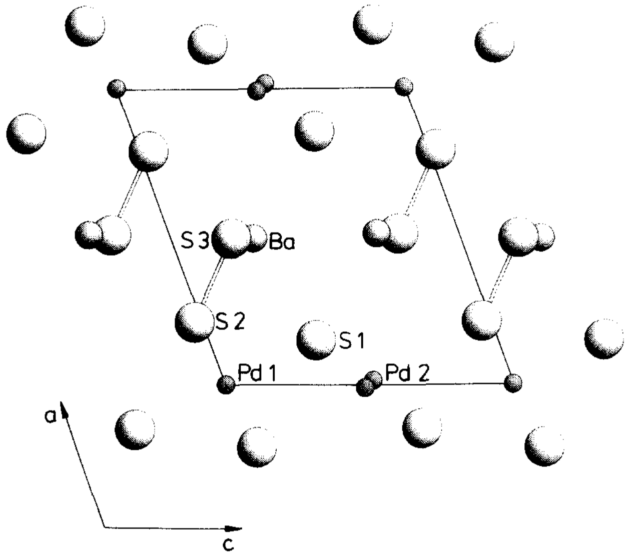

Fig. 1. $BaPd_2S_4$, *ac*-projection (cf. Table 2).

natively out of the plane. This is illustrated in Fig. 3 which gives an alternative perspective representation of the sulphur–palladium–sulphur layer already shown in Fig. 2. In this figure the atoms are plotted as spheres, the sulphur atoms S3, and the bonds are included. This arrangement corresponds to the formula $^2_\infty[PdS_{4/3}PdS_{2/3}\{\mu\text{-}(1,1)\text{-}S_2\}_{2/2}{}^{2-}]$.

As can be seen in Fig. 1 the palladium atoms Pd2 are alternatively 0.126(1) Å out of the plane formed by the sulphur atoms S1. The reason for this may be the relatively short distance of 3.107(3) Å between S2 and Pd2 at $y = 1/4$ and $y = 3/4$ respectively, and could

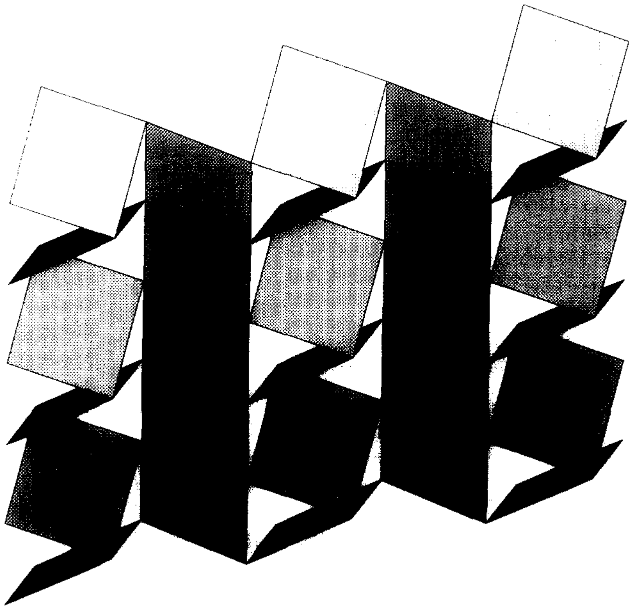

Fig. 2. Perspective representation of the square plane sulphur–palladium units.

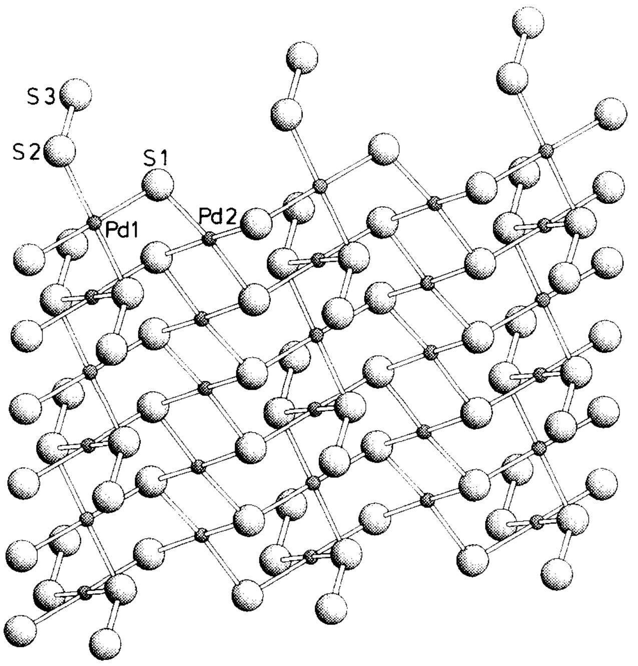

Fig. 3. Perspective view of the palladium–sulphur-layer.

be the result of a repulsion between the filled d_{z^2}-orbital of these palladium ions and the p-orbitals of these sulphur ions. This distortion gives rise to an angle of 171.38(5)° between the Pd2 atoms in the chain.

Each barium ion is coordinated by nine sulphur ions. Fig. 4 [10] shows the unusual polyhedron with C_s-symmetry (this symmetry, however, is far away from that of a threefold capped trigonal prism with D_{3h}-symmetry). Three of the sulphur atoms form a triangle. Parallel to this triangle four sulphurs, constituting 4/5 of a pentagon, lie in one plane with barium 0.390(2) Å underneath this plane. The fifth sulphur in the pentagon is 0.174(5) Å above the mentioned plane and is one end of the sulphur dumbbell whose second sulphur closes the polyhedron as the ninth apex. These polyhedrons share their square faces and build up a row following the symmetry of the 2_1-screw axis along [010]. Further edge-sharing of these rows leads to a plane of barium-centred polyhedrons.

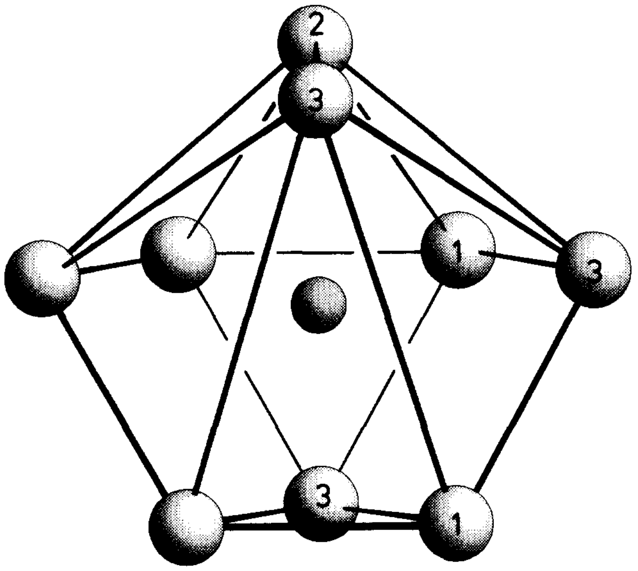

Fig. 4. Sulphur coordination polyhedron around barium (the sulphur atoms are labelled by their numbers (cf. Table 2)).

Acknowledgement

We wish to thank the Fonds der Chemischen Industrie for financial support.

References

[1] I.E. Grey and H. Steinfink, *J. Am. Chem. Soc., 92* (1970) 5093.
[2] J. Huster and W. Bronger, *J. Less-Common Met., 119* (1986) 159.
[3] J. Huster, *J. Less-Common Met., 84* (1982) 125.
[4] F. Gronvold, H. Haraldsen and A. Kjekshus, *Acta Chem. Scand., 14* (1960) 1879.
[5] P. Wselsky, *Ber. Wien, Akad., 60* (II) (1869) 263.
[6] E.J. Gabe, Y. Le Page, J.-P. Charland, F.L. Lee and P.S. White, NRCVAX – an interactive program system for structure analysis, *J. Appl. Crystallogr., 22* (1989) 384.
[7] W. Bronger und O. Günther, *J. Less-Common Met., 27* (1972) 73.
[8] H.-D. Wasel-Nielen and R. Hoppe, *Z. anorg. allg. Chem., 75* (1970) 209.
[9] E. Dowty, *ATOMS, IBM-PC Ver. 2.3*, 1993.