Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
OH3O—H1···O5	0.964	1.833	2.785 (3)	168.9
OH3O—H2···O12^{i}	0.971	1.993	2.932 (3)	162.3
OH3O—H3···O2^{ii}	1.001	1.910	2.902 (2)	170.5
O*W*1—H11···O10^{iii}	0.869	2.011	2.875 (2)	172.7
O*W*1—H12···O8^{iv}	0.806	2.097	2.828 (2)	150.8
O*W*2—H21···O7	0.891	1.814	2.690 (2)	167.1
O*W*2—H22···O8^{iv}	0.940	1.970	2.885 (2)	163.9
O*W*3—H31···O4^{v}	0.897	2.026	2.917 (2)	172.1
O*W*3—H32···O6^{iii}	0.819	1.971	2.785 (2)	171.9
O*W*4—H41···O11^{v}	0.886	1.945	2.815 (3)	167.0
O*W*4—H42···O14^{iv}	0.944	1.899	2.829 (2)	167.8
O*W*5—H51···O*W*2^{iii}	0.964	1.966	2.892 (2)	160.3
O*W*5—H52···O3^{iii}	0.818	1.835	2.639 (2)	167.2
O*W*6—H61···O9	0.981	1.953	2.913 (2)	165.4
O*W*6—H62···O*W*7	0.879	2.129	2.952 (3)	155.5
O*W*7—H71···O*W*8^{v}	0.838	1.909	2.715 (3)	161.1
O*W*7—H72···O13^{vi}	0.917	1.998	2.889 (3)	163.4
O*W*8—H81···O4	0.918	2.016	2.799 (3)	142.3
O*W*8—H82···O*W*5^{vii}	0.958	1.944	2.868 (3)	161.4

Symmetry codes: (i) $1-x, -1-y, 1-z$; (ii) $x, y-1, z$; (iii) $1-x, -y, -z$; (iv) $2-x, -y, -z$; (v) $2-x, 1-y, -z$; (vi) $x, 1+y, z$; (vii) $1+x, y, z$.

Water H atoms were found in a final difference Fourier map and included in the structure-factor calculations.

Data collection: *STADI*4 (Stoe & Cie, 1996*a*). Cell refinement: *STADI*4. Data reduction: *X-RED* (Stoe & Cie, 1996*b*). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997*a*). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*b*). Molecular graphics: *EUCLID* (Spek, 1982) and *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: KA1295). Services for accessing these data are described at the back of the journal.

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$Ag_2[Pd(NH_3)_2(SO_3)_2]$ powder

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Abstract

The water-insoluble title compound, disilver(I) diamminedisulfitopalladium(II), $Ag_2[Pd(SO_3)_2(NH_3)_2]$, was obtained from $Na_2[Pd(NH_3)_2(SO_3)_2]$ as a pale-green powder. *Ab initio* crystal structure determination was carried out using X-ray powder diffraction techniques. Patterson and Fourier syntheses were used for atom location, and Rietveld fitting was used for the final refinement. The structure consists of isolated flat *trans*-$[Pd(NH_3)_2(SO_3)_2]$ complexes, with SO_3 and Pd bonded through S. The Ag^+ cations are coordinated by distorted tetrahedra of O atoms from the SO_3 groups. Pd···Ag contacts of 3.296 (1) Å supplement the coordination of the Pd to octahedral, according to the (4 + 2) scheme. The substance is stable in air up to 448 K, after which it decomposes, yielding an Ag–Pd alloy of a solid solution and metallic Ag and Pd.

Comment

Heteronuclear complex compounds with a low decomposition temperature are often regarded as potential precursors for obtaining metal alloys. As there was some interest in Ag–Pd alloys, the available data on Ag–Pd complex compounds were investigated. The literature search revealed rather limited information on these compounds. References to syntheses of $Ag_2[Pd(NO_2)_4]$ (Chernyaev, 1964) and $Ag_2[Pd(C_2O_4)_2]$ (Gmelin, 1942), and to crystal structure data on Ag_2PdCl_4 (Schroder & Keller, 1988) were found.

The crystal structure of *trans*-$Ag_2[Pd(NH_3)_2(SO_3)_2]$, (I), is presented in Fig. 2. The structure can be defined as ionic, with separately located $[Pd(NH_3)_2(SO_3)_2]^{2-}$ anions. Complex ions are arranged in layers parallel to the *ab* plane, keeping an identical orientation. The shortest Pd···Pd distances are within the layers. The orientations of the complexes in two neighbouring parallel layers are related by 2_1 axes. Ag^+ cations are situated between the layers. The coordination of the Ag atom is provided by the O atoms of the SO_3 groups. AgO_4 tetrahedra may also be conditionally associated in layers where they are connected by apices. The sulfite groups are coordinated to the Pd atom through sulfur. The ligands have a planar centrosymmetrical arrangement around the Pd atom, with nearly right-angled (within errors) S—Pd—N corners. The bond lengths obtained for $[Pd(NH_3)_2(SO_3)_2]^{2-}$ do not differ significantly from those found for $Na_2[Pd(NH_3)_2(SO_3)_2]\cdot 6H_2O$ (Capparelli & Becka, 1969). Some lengthening of the Pd—S bond to 2.288 Å, in comparison with 2.245 Å in $[Pd(NH_3)_3(SO_3)]$ (Spinnler & Becka, 1967), is considered to be the consequence of the '*trans* effect'. There are no data on a compound with three sulfite groups, but for $Na_6[Pd(SO_3)_4]$, the increase in Pd—S distances up to 2.316–2.341 Å was found by Messer *et al.* (1981). The geometry of the sulfite groups does not undergo significant distortions, although their O atoms are coordinated by Ag^+ ions and participate in the formation of hydrogen bonds. Comparing (I) and $Na_2[Pd(NH_3)_2(SO_3)_2]\cdot 6H_2O$ (Capparelli & Becka, 1969), it is possible to note a rather close similarity between the orientations of the sulfite groups. The O1—S—Pd—N torsion angles in the Ag and Na compounds are 78 and 79°, respectively. This fact may be considered as the absence of freedom of rotation of the sulfite groups in the plane of the complex. The Ag^+ cation has distorted tetrahedral O coordination. Four different complexes are involved to form the $[AgO_4]$ group. Although the Ag—O distances observed (average value 2.41 Å) exceed the distances described in the literature (Wells, 1984) by approximately 0.2–0.3 Å, they are undoubtedly within the range of chemical bonding. Thus, the compound as a whole should be classified as a double-complex compound.

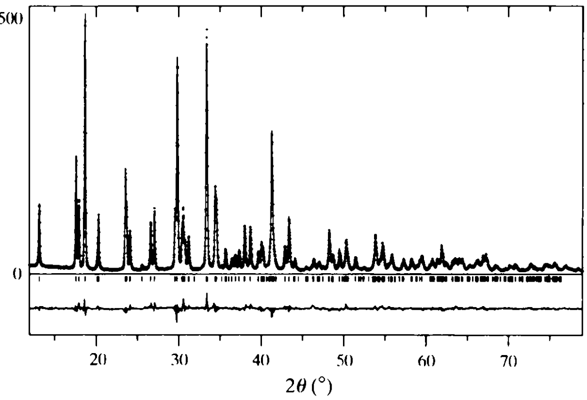

Fig. 1. Observed (dots), calculated (superimposed line) and difference profiles for (I), after the Rietveld refinement. The reflection positions are marked by ticks.

The Ag atoms can be considered in one further configuration. Since they are arranged at 3.296 Å from the Pd atom above and below the complex plane, they complete the Pd^{II} coordination according to the (4 + 2) scheme (Wells, 1984), implying the presence of two additional contacts more distant than the four main bonds. The Pd···Ag distance here is less than the value of 3.715 Å in Ag_2PdCl_4 (Schroder & Keller, 1988), but it is still larger than the sum of the atomic radii.

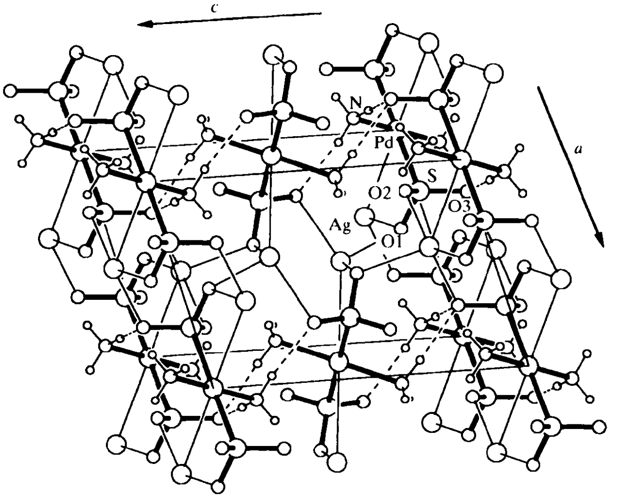

Fig. 2. The crystal structure of $Ag_2[Pd(NH_3)_2(SO_3)_2]$.

Experimental

The synthesis of (I) consisted of two stages:

$$trans\text{-}[Pd(NH_3)_2Cl_2] + 2Na_2SO_3 \rightarrow trans\text{-}Na_2[Pd(NH_3)_2(SO_3)_2] + 2NaCl \quad (1)$$

$$trans\text{-}Na_2[Pd(NH_3)_2(SO_3)_2] + 2AgNO_3 \rightarrow trans\text{-}Ag_2[Pd(NH_3)_2(SO_3)_2] + 2NaNO_3 \quad (2)$$

The chemical reactions were carried out at room temperature. Initially, *trans*-$[Pd(NH_3)_2Cl_2]$ was suspended in a small amount of water and Na_2SO_3 was added, with 10% excess. White $Na_2[Pd(NH_3)_2(SO_3)_2]\cdot 6H_2O$ precipitated from the solution. It was filtered and then washed in small amounts of cold water and alcohol. The $Na_2[Pd(NH_3)_2(SO_3)_2]$ product was then dissolved in a small volume of water at 323–333 K and $AgNO_3$ was added under intensive agitation. A pale-green precipitate, (I), was formed, which was washed with water and then with alcohol. According to the chemical analysis, this final product had the following composition: $Ag_{2.01}Pd_{1.01}(NH_3)_{1.96}(SO_3)_{1.98}$. Thermal analysis showed that the substance was stable in air up to 448 K and then decomposed, yielding an Ag–Pd alloy of a solid solution, and metallic Ag and Pd. The sample was prepared by top-loading the standard quartz sample holder and removing the excess of well-grained substance.

Crystal data

$Ag_2[Pd(SO_3)_2(NH_3)_2]$
$M_r = 516.33$
Monoclinic
$P2_1/c$
$a = 7.0518(1)$ Å
$b = 5.8510(1)$ Å
$c = 10.3799(2)$ Å
$\beta = 108.220(1)°$
$V = 406.80(3)$ Å^3
$Z = 2$

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
$T = 293$ K
Specimen shape: circular flat plate
20 × 20 × 0.5 mm
Cooling rate: 0 K min^{-1}
Specimen prepared at 101 kPa and 293 K
Particle morphology: thin powder
Pale yellow

Data collection

DRON-4 powder diffractometer
$\theta/2\theta$ scan
Specimen mounting: packed powder pellet
Specimen mounted in reflection mode

$T = 293$ K
330 measured reflections
$\theta_{max} = 45°$
$2\theta_{min} = 12$, $2\theta_{max} = 90°$
Increment in $2\theta = 0.02°$

Refinement

Refinement on F^2
$R_p = 0.057$
$R_{wp} = 0.074$
$R_{exp} = 0.044$
$R_B = 0.043$
Wavelength of incident radiation: 1.54056 Å
Excluded region(s): none
Data reduction: none
Profile function: Pearson VII
41 parameters

H-atom parameters constrained
Weighting scheme based on measured s.u.'s
Extinction correction: none
Preferred orientation correction: March–Dollase correction
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Pd	0	0	0	0.26 (8)
Ag	0.4396 (2)	−0.2340 (3)	0.1478 (1)	1.36 (7)
S	0.2515 (6)	0.2626 (8)	0.0358 (1)	0.2 (1)
O1	0.443 (1)	0.174 (2)	0.1161 (9)	0.3 (1)
O2	0.214 (1)	0.464 (2)	0.1134 (8)	0.3 (1)
O3	0.254 (1)	0.355 (1)	−0.096 (1)	0.3 (1)
N	−0.096 (1)	0.157 (1)	0.1485 (9)	0.6 (3)

Table 2. *Selected geometric parameters (Å, °)*

Pd—N	2.078 (9)	Ag—O3^{iii}	2.49 (1)
Pd—S	2.288 (5)	S—O1	1.45 (1)
Pd—Ag	3.296 (1)	S—O2	1.50 (1)
Ag—O1	2.41 (1)	S—O3	1.48 (1)
Ag—O1^{i}	2.390 (9)	N—O3^{iv}	3.05 (1)
Ag—O2^{ii}	2.332 (9)	N—O3^{v}	3.00 (1)
Pd—S—O1	113.0 (8)	O1—S—O3	113 (1)
Pd—S—O2	110.8 (7)	O2—S—O3	105 (1)
Pd—S—O3	109.1 (7)	Pd—N—O3^{iv}	117.8 (7)
N—Pd—S	89.9 (5)	Pd—N—O3^{v}	106.1 (7)
O1—S—O2	105 (1)	O3^{iv}—N—O3^{v}	109.3 (6)

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

Since the title compound was only available as a powder, the structure determination was carried out using X-ray powder diffraction. The experimental data were collected on the DRON-4 automatic diffractometer in the X-ray Structure Analysis Laboratory of the Institute of Chemistry and Chemical Technology, Krasnoyarsk, equipped with a secondary flat graphite monochromator, in conjunction with a scintillation detector. Cu $K\alpha$ radiation was used ($\lambda_1 = 1.54056$, $\lambda_2 = 1.54439$ Å). The diffraction pattern was scanned in steps of 0.02° in 2θ with a count time of 10 s per step, over the most informative angular range of 12–90% (2θ), at ambient temperature. Corundum was used as the external standard. The powder pattern of $Ag_2[Pd(NH_3)_2(SO_3)_2]$ is presented in Fig. 2. The X-ray powder diffraction data have been deposited in the JCPDS–ICDD PDF2 database. The initial data processing, including peak location, was carried out with the help of the *XDIG* program (Solovyov, 1998). Cell parameters were obtained from the *d* spaces by indexing and refining, using programs described by Visser (1969) and Kirik *et al.* (1979). The space group was determined from analysis of the systematic absences. The structural investigations were carried out using a full-profile structure analysis package (Solovyov, 1998), based on a modified version of the Rietveld refinement program *DBWS*-9006*PC* (Wiles & Young, 1981). The intensities of 330 reflections were estimated from the powder pattern by means of the full-profile fitting procedure and used in the Patterson synthesis. Atoms of Ag, Pd and S were located directly from the Patterson map. The positions of the light atoms (O and N) were defined from a difference Fourier synthesis. H atoms were not located, but they were included in the refined structure model and rigidly connected to their N atoms during the refinement. The idealized model of the NH_3 group was used, with H—N—H and Pd—N—H angles of 109°, and N—H distances of 0.9 Å. Analysis of the interatomic distances and angles revealed two possible hydrogen bonds between N and O, which enabled us to determine the orientation of the NH_3 groups in the N—Pd—S plane. The final refinement was carried out by the Rietveld method (Rietveld, 1969).

Data collection: DRON-4 local data collection software. Cell refinement: *DBWM* (Solovyov, 1998), local modification of *DBWS*-9006*PC* (Wiles & Young, 1981). Data reduction: *XDIG* (Solovyov, 1998). Program(s) used to solve structure: local programs (Patterson and Fourier syntheses). Program(s) used to refine structure: *DBWM*. Molecular graphics: *XP* (Siemens, 1989).

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: AV1026). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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