0·075 (6) and 0·566 (5) Å, respectively, from the plane.

The only direct hydrogen bonding between complexes occurs in the *c* direction, from the NH_2 group of one ligand to the alkoxide O of a ligand from a neighbouring molecule. The N···O distance is 2·951 (5) Å, the magnitude normally found for N···O hydrogen bonds. The Cu···Cu distance between complexes is 5·164 Å (*c*/2).

The compound contains one molecule of water of crystallization per formula unit, with O(*W*) on a twofold axis. This causes additional hydrogen bonding which connects complexes that have Cu atoms on the same (200) plane. The O(*W*)···N and O(*W*)···O(1) distances of 3·024 (7) and 2·706 (6) Å are normal values for O···N and O···O hydrogen-bond contacts. Fig. 2 depicts the crystal structure and Table 3 gives the hydrogen-bond parameters.

The hydrogen-bonding network differs from that found for the dichelate complex cation $[Cu(C_4H_{10}NO)(C_4H_{11}NO)(H_2O)]_2^{2+}$ in which the same amino-alcohol is the ligand (Bertrand, Fujita & Vanderveer, 1980). This cation is a hydrogen-bonded dimer with a short O···O distance of 2·516 (3) Å between pairs of ligands coordinated to different Cu atoms. All other hydrogen-bond donor–acceptor distances in the compound are normal. Since all hydrogen-bond contacts in $[Cu(C_4H_{10}NO)_2].H_2O$ are normal, the complex is to be regarded as monomeric.

In $[Cu(C_4H_{11}NO)_2](C_7H_5O_2)_2$ (Muhonen & Hämäläinen, 1978) the complex ions are connected by hydrogen bonds involving the benzoate ions. The Cu···Cu distance is 5·654 (2) Å and there is a short O···O distance of 2·431 (7) Å between the ligand and the benzoate ion.

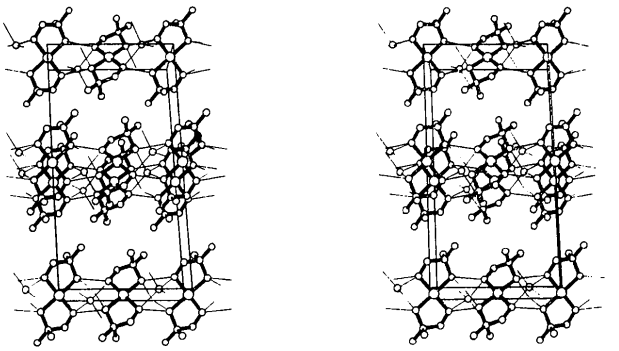

Fig. 2. Stereoview of overall structure. Fine lines indicate hydrogen bonds. The *a* axis is up the page, *b* towards the viewer, and *c* across from left to right.

Table 3. *Hydrogen-bond distances* (Å) *and angles* (°)

D–H···*A*	∠*D*–H···*A*	*D*···*A*	H···*A*	*D*–H
N–H(9)···O(1^{ii})	169 (5)	2·951 (5)	2·07 (5)	0·89 (5)
N–H(10)···O(*W*^{iii})	170 (4)	3·024 (7)	2·29 (5)	0·75 (5)
O(*W*)–H(11)···O(1)	167 (6)	2·706 (6)	1·91 (6)	0·81 (6)

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

References

BERTRAND, J. A., FUJITA, E. & VANDERVEER, D. G. (1980). *Inorg. Chem.* **19**, 2022–2028.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

MUHONEN, H. (1980). *Finn. Chem. Lett.* pp. 138–141.

MUHONEN, H. & HÄMÄLÄINEN, R. (1978). *Acta Chem. Scand. Ser. A*, **32**, 121–125.

STEWART, J. M., MACHIN, P. A., DICKINSON, C., AMMON, H. L., HECK, H. & FLACK, H. (1976). The XRAY 76 system. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland.

Acta Cryst. (1981). B**37**, 953–956

Tetrakis(dimethyl sulphoxide)palladium(II) Bis(tetrafluoroborate) Dimethyl Sulphoxide Solvate

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Abstract. $C_{10}H_{30}B_2F_8O_5PdS_5$, $[Pd\{(CH_3)_2SO\}_4][BF_4]_2.(CH_3)_2SO$, monoclinic, $P2_1/c$, $a = 10·650$ (3), $b = 14·163$ (5), $c = 17·778$ (7) Å, $\beta = 95·85$ (3)°, $U = 2667·6$ Å^3, $Z = 4$, $D_c = 1·67$ Mg m^{-3}, μ(Cu $K\alpha$) = 9·95 mm^{-1}; final $R = 0·086$ for 2475 unique diffractometer data. The Pd^{II} atom displays the expected four-coordinate square-planar geometry. Two of the co-ordinated dimethyl sulphoxide (Me_2SO) ligands bond to the metal *via* S and the other two *via* O atoms. The dication exhibits a *cis* geometry. The anions and the Me_2SO solvate molecule are not coordinated.

Introduction. Dimethyl sulphoxide is an interesting ligand because of the coordination isomerism which it

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exhibits. Small or highly charged metal ions favour coordination *via* the O atom whereas large or less highly charged metal ions tend to favour S-bonding. The dication $[Pd(Me_2SO)_4]^{2+}$ is of special interest because it is considered to contain two S-bonded and two O-bonded ligands in a *cis* arrangement (Wayland & Schramm, 1968). However, the ^1H NMR spectrum of this dication shows a temperature variation indicating that several isomers exist, at least in solution (Wayland & Schramm, 1968; Price, Schramm & Wayland, 1970). To confirm the postulation of the structure in the solid state this single-crystal X-ray analysis was undertaken.

The title compound was prepared by dissolving palladium chloride in Me_2SO, at elevated temperatures, and adding an acetone solution containing a stoichiometric amount of silver tetrafluoroborate. The solution was filtered and, upon cooling, the filtrate yielded yellow platelets. The crystals were air-sensitive and were mounted in 0·5 mm Lindemann tubes under nitrogen. 4107 intensities were measured for $3{\cdot}0 < 2\theta \leq 130{\cdot}0°$ on a Syntex $P2_1$ four-circle diffractometer with graphite-monochromated Cu $K\alpha$ radiation, an ω–2θ scan technique, and a crystal 0·56 × 0·19 × 0·08 mm. Lp corrections and a numerical absorption correction using the indexed faces of the crystal [(010), (0$\bar{1}$0), (100), ($\bar{1}$00), (001) and (00$\bar{1}$)] were applied; transmission factors ranged from 0·278 to 0·513. The data were averaged to give 2475 unique observed intensities [$F > 4\sigma(F)$]. Cell dimensions were derived from the angular measurement of 15 strong reflections in the range $35 < 2\theta < 50°$.

The Pd atom was located from a Patterson synthesis, and all the other non-H atoms were found from subsequent difference syntheses. The structure was refined by full-matrix least squares. The Pd, S, O, and C atoms of the cation were assigned anisotropic thermal parameters; the methyl H atoms were not located. The atoms of the Me_2SO solvate molecule and the B atoms of the anions were assigned isotropic temperature factors while the F atoms were assigned a common isotropic temperature factor. Both BF_4^- groups were disordered; each was treated as a B atom surrounded by two interlocking tetrahedra of F atoms. In each tetrahedron the B–F and F···F distances were fixed at 1·37 and 2·237 Å respectively; the occupancies of the F atoms were refined as k and $(1-k)$. Complex neutral-atom scattering factors (*International Tables for X-ray Crystallography*, 1974) were employed, with the weighting scheme $w = 2{\cdot}4472/[\sigma^2(F) + 0{\cdot}002F^2]$ for the final stages of refinement. The final $R = 0{\cdot}086$ and $R' = \sum w^{1/2}\Delta/\sum w^{1/2}|F_o| = 0{\cdot}091$. Final atomic

Table 1. *Atom coordinates* ($\times 10^4$) *and isotropic or equivalent isotropic temperature factors* ($Å^2 \times 10^3$)

	x	y	z	U
Pd(1)	7080 (1)	1841 (1)	2125 (1)	47 (1)
S(1)	5271 (4)	2017 (3)	2651 (2)	59 (2)
S(2)	6407 (4)	2616 (3)	1055 (2)	64 (2)
S(3)	9681 (4)	2220 (3)	1430 (3)	68 (3)
S(4)	9026 (4)	1036 (3)	3416 (2)	66 (3)
O(1)	4281 (12)	2611 (11)	2270 (7)	90 (9)
O(2)	7303 (13)	2567 (11)	486 (7)	99 (9)
O(3)	8780 (9)	1504 (7)	1733 (6)	55 (6)
O(4)	7604 (10)	1038 (8)	3074 (6)	66 (6)
C(1)	4686 (19)	881 (14)	2766 (12)	89 (13)
C(2)	5613 (18)	2392 (15)	3608 (10)	83 (12)
C(3)	6097 (19)	3823 (12)	1257 (12)	89 (13)
C(4)	4951 (18)	2179 (15)	659 (11)	87 (12)
C(5)	10190 (18)	1635 (13)	638 (12)	85 (13)
C(6)	11074 (18)	2086 (17)	2102 (15)	113 (16)
C(7)	9348 (22)	−200 (13)	3463 (12)	95 (13)
C(8)	8926 (22)	1258 (18)	4411 (11)	107 (15)
B(1)	2646 (9)	1174 (8)	4664 (7)	135 (12)
F(1)	3887 (10)	904 (15)	4763 (12)	161 (4)
F(1*a*)	3841 (14)	1318 (24)	4465 (19)	161 (4)
F(2)	2505 (18)	1894 (12)	4147 (11)	161 (4)
F(2*a*)	2212 (29)	1989 (16)	4961 (20)	161 (4)
F(3)	2277 (18)	1477 (15)	5339 (9)	161 (4)
F(3*a*)	2669 (33)	469 (20)	5192 (17)	161 (4)
F(4)	1916 (17)	423 (12)	4405 (12)	161 (4)
F(4*a*)	1864 (26)	921 (24)	4037 (14)	161 (4)
B(2)	−1572 (9)	3999 (9)	3218 (7)	101 (8)
F(5)	−950 (25)	3268 (15)	2913 (17)	157 (4)
F(5*a*)	−1232 (19)	3576 (16)	2576 (10)	157 (4)
F(6)	−2844 (10)	3907 (25)	3022 (15)	157 (4)
F(6*a*)	−2707 (13)	4448 (17)	3058 (13)	157 (4)
F(7)	−1329 (26)	3983 (27)	3989 (7)	157 (4)
F(7*a*)	−670 (16)	4645 (15)	3474 (14)	157 (4)
F(8)	−1165 (29)	4838 (12)	2946 (20)	157 (4)
F(8*a*)	−1678 (21)	3328 (15)	3763 (12)	157 (4)
S(5)	6416 (10)	−533 (8)	892 (6)	59 (3)
C(101)	7575 (21)	−900 (17)	1523 (14)	110 (8)
C(102)	7235 (23)	−183 (18)	205 (15)	122 (9)
O(100)	5876 (17)	151 (14)	1161 (11)	144 (7)

$U_{eq} = [3 \sin\alpha \sin\beta \sin\gamma]^{-1}\{U_{11} \sin\alpha/\sin\beta^* \sin\gamma^* + \cdots + U_{12} \sin 2\gamma/\sin^2\gamma^*\}$.

Table 2. *Bond lengths* (Å) *and angles* (°)

S(1)–Pd(1)	2·240 (4)	S(2)–Pd(1)	2·249 (4)
O(3)–Pd(1)	2·061 (9)	O(4)–Pd(1)	2·065 (10)
O(1)–S(1)	1·460 (13)	C(1)–S(1)	1·745 (18)
C(2)–S(1)	1·783 (17)	O(2)–S(2)	1·461 (13)
C(3)–S(2)	1·784 (17)	O(3)–S(3)	1·531 (10)
C(4)–S(2)	1·749 (18)		
C(5)–S(3)	1·766 (18)	C(6)–S(3)	1·817 (20)
O(4)–S(4)	1·573 (11)	C(7)–S(4)	1·783 (18)
C(8)–S(4)	1·810 (18)	C(101)–S(5)	1·664 (25)
C(102)–S(5)	1·648 (27)	O(100)–S(5)	1·246 (20)
S(2)–Pd(1)–S(1)	94·9 (2)	O(3)–Pd(1)–S(1)	171·7 (3)
O(3)–Pd(1)–S(2)	92·4 (3)	O(4)–Pd(1)–S(1)	83·8 (3)
O(4)–Pd(1)–S(2)	175·3 (3)	O(4)–Pd(1)–O(3)	88·6 (4)
O(1)–S(1)–Pd(1)	118·8 (5)	C(1)–S(1)–Pd(1)	106·2 (7)
C(1)–S(1)–O(1)	109·6 (9)	C(2)–S(1)–Pd(1)	109·3 (6)
C(2)–S(1)–O(1)	109·8 (9)	C(2)–S(1)–C(1)	101·7 (10)
O(2)–S(2)–Pd(1)	112·8 (5)	C(3)–S(2)–Pd(1)	110·3 (7)
C(4)–S(2)–Pd(1)	111·1 (5)	C(4)–S(2)–O(2)	108·7 (7)
C(3)–S(2)–O(2)	109·4 (9)	C(5)–S(3)–O(3)	103·0 (7)
C(4)–S(2)–C(3)	104·2 (10)		
C(6)–S(3)–O(3)	101·5 (10)	C(6)–S(3)–C(5)	100·3 (11)
C(7)–S(4)–O(4)	101·1 (9)	C(8)–S(4)–O(4)	103·1 (9)
C(8)–S(4)–C(7)	98·9 (11)	S(3)–O(3)–Pd(1)	124·7 (6)
S(4)–O(4)–Pd(1)	119·1 (6)	C(102)–S(5)–C(101)	100·4 (13)
O(100)–S(5)–C(101)	108·9 (14)	O(100)–S(5)–C(102)	110·5 (15)

coordinates, and equivalent isotropic and isotropic temperature factors are given in Table 1; the F atoms denoted *a* refer to the second set of disordered F atoms. The bond lengths and angles associated with these atomic coordinates are listed in Table 2.*

Discussion. Fig. 1 shows the unit-cell contents. There are no abnormally close contacts between the atoms of the cation, anions, and the solvent molecule. The shortest intermolecular distance is 3·137 (25) Å between O(100) and C(4) related by the symmetry operation $x, \frac{1}{2}-y, \frac{1}{2}+z$.

The Pd atom displays the expected four-coordinate square-planar geometry (Fig. 2). Two of the coordinated Me_2SO ligands bond to the metal *via* their S atoms, and the others through O. They are arranged so that the ligands with the same donor atom are *cis* to each other. The angles at the Pd atom show small deviations from the idealized value of 90°, with the widest angle between the two S-bonded ligands and the narrowest between the two O-bonded groups. The presence of both S- and O-bonded Me_2SO ligands in the same molecule has been established by crystallographic techniques in several Ru complexes (Mercer & Trotter, 1975; Davies, Einstein, Farrell, James & McMillan, 1978). The *cis* arrangement of the ligands in this complex may be attributed to the fact that S-bonded Me_2SO is considered to be a weak π-acceptor ligand, while O-bonded Me_2SO is a strong σ donor, so there would be little competition for the metal π electrons with the S- and O-bonded groups *trans* to each other.

The two Pd–S distances in the title compound are equivalent. They lie in the range [2·231 (3)–2·253 (3) Å] found in the structure of *cis*-$Pd(NO_3)_2(Me_2SO)_2$ (Langs, Hare & Little, 1967) where the Me_2SO ligands are *trans* to monodentate nitrate groups, but are significantly shorter than the equivalent lengths of 2·300 (4) Å observed in *trans*-$PdCl_2(Me_2SO)_2$ (Bennett, Cotton & Weaver, 1966). There are no other examples of O-bonded Me_2SO to Pd, but the Pd–O distances in the title compound are in close agreement with the 2·066 (8) Å for the Pd–O(nitrate) bonds in *cis*-$Pd(NO_3)_2(Me_2SO)_2$ (Langs, Hare & Little, 1967).

All four S atoms in the cation have distorted tetrahedral coordination geometries. For S(3) and S(4), which are not involved in bonding to the metal, one coordination site is occupied by the lone pair of electrons, and the O–S–C and C–S–C angles are significantly smaller than the idealized tetrahedral value. For the metal-coordinated atoms, S(1) and S(2), the Pd–S–O angles are the widest [mean 115·8 (6)°], and the S–O distance [mean 1·461 (13) Å] is shorter than the distance [1·531 (15) Å] in the free ligand (Thomas, Shoemaker & Eriks, 1966). This distance is very similar to the 1·463 (7) Å in $Pd(NO_3)_2(Me_2SO)_2$ (Langs, Hare & Little, 1967) and is evidence for considerable $d\pi$–$p\pi$ bonding. Short S–O distances, concomitant with long Ru–S distances in $[NH_2Me_2][RuCl_3(Me_2SO)_3]$ (McMillan, Mercer, James & Trotter, 1975), have been attributed to a decrease in the possible $d\pi$–$p\pi$ back donation from the Ru to the S atom caused by the competition from the other ligands for the available π-donor orbitals.

The S–O distances of the O-coordinated Me_2SO ligands are *ca* 0·09 Å longer than for the S-bonded ligands. This reflects the decrease in π bonding in these bonds upon coordination of the O atom to the metal. These S–O distances found in this study are similar to the value of 1·557 (4) Å reported for the O-coordinated Me_2SO group in $Ru(Me_2SO)_4Cl_2$ (Mercer & Trotter, 1975).

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35875 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

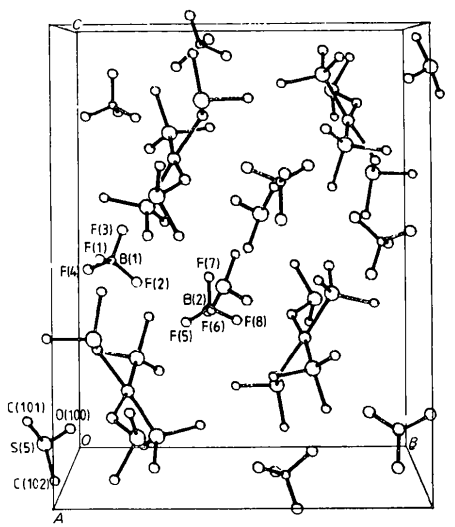

Fig. 1. The unit-cell contents for $[Pd(Me_2SO)_4][BF_4]_2.(CH_3)_2SO$.

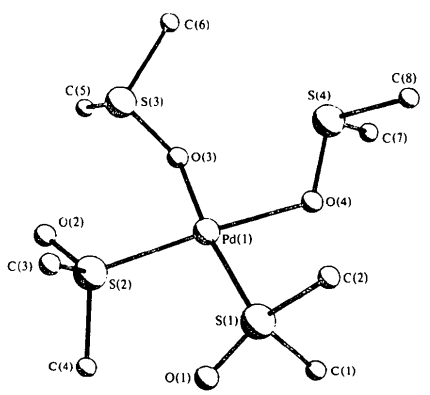

Fig. 2. The geometry of the $[Pd(Me_2SO)_4]^{2+}$ cation.

The S–C lengths and C–S–C angles correspond closely to values reported in other Me_2SO complexes. The bond parameters in the uncoordinated solvent Me_2SO molecule have fairly high e.s.d.'s, but the values do not deviate significantly from those in the free ligand (Thomas, Shoemaker & Eriks, 1966). The BF_4^- anions are disordered and the bond parameters have been fixed at the idealized values.

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References

BENNETT, M. J., COTTON, F. A. & WEAVER, D. L. (1966). *Nature* (*London*), pp. 286–287.

DAVIES, A. R., EINSTEIN, F. W. B., FARRELL, N. P., JAMES, B. R. & MCMILLAN, R. S. (1978). *Inorg. Chem.* **17**, 1965–1969.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

LANGS, D. A., HARE, C. R. & LITTLE, R. G. (1967). *J. Chem. Soc. Chem. Commun.* pp. 1080–1081.

MCMILLAN, R. S., MERCER, A., JAMES, B. R. & TROTTER, J. (1975). *J. Chem. Soc. Dalton Trans.* pp. 1006–1010.

MERCER, A. & TROTTER, J. (1975). *J. Chem. Soc. Dalton Trans.* pp. 2480–2483.

PRICE, J. H., SCHRAMM, R. F. & WAYLAND, B. B. (1970). *J. Chem. Soc. Chem. Commun.* pp. 1377–1378.

SHELDRICK, G. M. (1976). *SHELX* 76. Program for crystal structure determination. Univ. of Cambridge, England.

THOMAS, R., SHOEMAKER, C. R. & ERIKS, K. (1966). *Acta Cryst.* **21**, 12–20.

WAYLAND, B. B. & SCHRAMM, R. F. (1968). *J. Chem. Soc. Chem. Commun.* pp. 1465–1466.