Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: LI1149). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). **C52**, 2188–2191

Bis[bis(2-pyridyl-*N*) sulfide]palladium(II) Bis(tetrafluoroborate)

Francesco Nicolò, Giuseppe Bruno and Giuseppe Tresoldi

Dipartimento di Chimica Inorganica, Analitica e Struttura Molecolare, Universitá degli Studi di Messina, Via Salita Sperone 31, I-98166 Vill. S. Agata, Messina, Italy. E-mail: nicolo@medif0.unime.it

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Abstract

The title compound, $[Pd(dps)_2](BF_4)_2$ (dps = di-2-pyridyl sulfide, $C_{10}H_8N_2S$), has been synthesized by the reaction of dps with the solvated species $[Pd(L_2)(acetone)_2](BF_4)_2$ (L = 1,5-cyclooctadiene) at low temperature. Its structure has been determined by X-ray diffraction. In the $[Pd(dps)_2]^{2+}$ cation, the Pd atom lies on a crystallographic inversion centre and exhibits a square-planar geometry involving four pyridine N atoms of both dps molecules acting as chelating ligands [Pd—N1 2.032 (2) and Pd—N2 2.026 (3) Å]. The two equal six-membered chelate rings are in boat conformations.

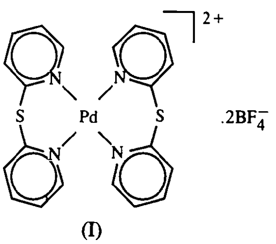
Comment

As a continuation of our investigation on the coordination chemistry of flexible bipyridine-like ligands (Tresoldi, Piraino, Rotondo & Faraone, 1991; Tresoldi, Rotondo, Piraino, Lanfranchi & Tiripicchio, 1992; De Munno *et al.*, 1993; Bruno, Nicolò, Lo Schiavo, Sinicropi & Tresoldi, 1995), we have examined the reactions of di-2-pyridyl sulfide (dps) with solvated species formed *in situ* by the reaction of the palladium(II)–diene or platinum(II)–diene complexes. Recently, some crystal structure determinations (Tresoldi *et al.*, 1992; De Munno *et al.*, 1993; Bruno *et al.*, 1995) have shown that the chelate ring of coordinated flexible bipyridine-like ligands adopts a boat conformation in the solid state, while NMR studies have shown that these flexible ligands favour dynamic processes in solution (Tresoldi *et al.*, 1991, 1992; De Munno *et al.*, 1993). Concerning dps and its derivatives, it is known that the free dps ligand adopts three planar (*N*,*N*-inside, *N*,*N*-outside, *N*-inside/*N*-outside) and several twisted conformations in the three states of matter (Chachaty, Pappalardo & Scarlata, 1976; Amato, Bandoli, Grassi, Pappalardo & Scarlata, 1989; Bombieri, Forsellini & Graziani, 1978; Colonna, Distefano, Galasso, Pappalardo & Scarlata, 1977) which may be present when dps is bonded to the metal as a chelate or bridging ligand. The route followed for the synthesis of the dicationic complexes $[M^{II}(dps)_2](BF_4)_2$ [M = Pd, (I), and Pt, (II)] is

$$M(L)_2Cl_2 + 2AgX \rightarrow [M(L)_2(solvent)_2]X_2$$

$$[M(L)_2(solvent)_2]X_2 + 2dps \rightarrow [M(dps)_2]X_2$$

where M is Pd or Pt, L is 1,5-cyclooctodiene or dicyclopentadiene, and X is BF_4^- or PF_6^-. The procedure involves the *in situ* formation of solvated species followed by the displacement of the diene and the coordinated solvent by dps. The final reactions proceed slowly at 255 K and complexes (I) and (II) are obtained in high yields, whereas at higher temperature, large decomposition occurs.



(I)

Dissolving (I) in boiling methanol and filtering to eliminate black powder allowed a highly crystalline product to be obtained. The compounds are white, stable for several months in the solid state and slightly soluble in methanol at 323 K and stable for several days. The IR spectra of (I) and (II) show a very strong band in the range 1590–1594 cm^{-1} and two in the range

763–788 cm^{-1}, which is characteristic of the dps ligand (Tresoldi *et al.*, 1991, 1992; De Munno *et al.*, 1993; Bruno *et al.*, 1995). Although the too low solubility in all common solvents prevents the recording of the NMR spectra of (I) and (II) at room temperature, in CD_3OD at 323 K, the ^1H NMR spectrum of (I) shows signals for the *ortho* and *meta* pyridine protons (near the S atom) as broad multiplets partially overlapped in the range δ8.33–8.27, while those of (II) are in the range δ 8.77–8.70. The signals of the *para* and *meta* protons are well resolved in both compounds at δ 8.22 and 7.54 [for (I)] and δ 8.61 and 7.92 [for (II)]. Furthermore, the ^{13}C NMR spectrum of (I) under the same conditions shows the *ortho* and *para* pyridine C-atom signals at δ 155.6 and 144.1, and other C atoms at δ 132.1 and 128.1. The quaternary C-atom signal is not observed.

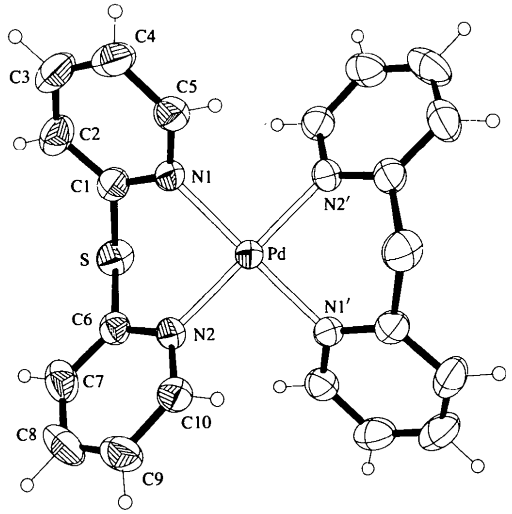


Fig. 1. Perspective view of the title compound showing the labelling scheme of its asymmetric unit (shaded atoms). Displacement ellipsoids are drawn at the 50% probability level and the BF_4^- anion has been omitted for clarity.

The solid-state structure is constituted by palladium complex cations and tetrafluoroborate anions in a 1:2 ratio for charge balance. The crystal packing seems to be mainly determined by several hydrogen-bond interactions of the tetrafluoroborate F atoms with the dps H atoms (F···H_{py} contacts range from 2.4 to 2.8 Å). The metal atom is on a crystallographic inversion centre and displays an almost perfect square-planar coordination geometry. The two Pd—N distances are equal within experimental error [2.032 (2) *versus* 2.026 (3) Å], while the N—Pd—N angles of adjacent N atoms are close to the ideal value, although the angle corresponding to the ligand byte is slightly smaller than that between the two dps ligands [88.93 (9) *versus* 91.07 (9)°]. The Pd(dps) fragment is very similar to the corresponding one in the neutral compound [Pd(dps)Cl_2] which we have already studied (Tresoldi *et al.*, 1992). The byte of the chelating ligand with the metal centre forms a six-membered coordination ring showing a cyclohexane-like conformation. The puckering analysis (Cremer & People, 1975) confirmed the 'boat' conformation of the ring [θ = 89.5 (1), φ = 179.0 (1)° and Q = 1.055 (8) Å]; the C and N atoms lie on a plane from which the Pd and S atoms deviate by 0.929 (1) and 0.901 (1) Å on the same side, respectively. Due to the crystallographic site symmetry, the two chelate rings are inverted with respect to one another and the dps S atoms lie on opposite sides with respect to the Pd coordination mean plane.

The dps ligand acts as a chelating ligand, adopting a bent butterfly-like conformation as usually observed for coordinated (Tresoldi *et al.*, 1992) and free (Amato *et al.*, 1989) compounds, while the planar arrangement is revealed for the N-protonated species (Bombieri *et al.*, 1978) due to the hydrogen bond between the two N atoms. The two 2-pyridyl ring planes [dihedral angle 66.4 (1)°] form equal dihedral angles [48.57 (9) *versus* 48.20 (8)°] with the Pd coordination mean plane, within experimental error. Statistical analysis of analogous structures reported in the Cambridge Structural Database (Allen *et al.*, 1991) has shown the strict correlation between the size of the dps chelating byte (distance N···N) and the average N—C_{py}—S—C_{py} torsion angle; the correlation coefficient was 0.97 for eleven ligands.

Experimental

Di-2-pyridyl sulfide (Chachaty *et al.*, 1976) and [Pd(1,5-C_8H_{12})Cl_2] (Drew & Doyle, 1972) were prepared according to published methods. All other reagents and solvents are commercial products. Elemental analyses were carried out at the Redox Microanalytical Laboratory of Cologno Monzese, Milan. IR spectra were recorded on an FT-IR 1720X spectrophotometer (nujol mulls using CsI plates) and the ^1H and ^{13}C NMR spectra were recorded on a Bruker AMX 300 spectrometer. $[Pd(dps)_2](BF_4)_2$ was prepared from an acetone solution (20 ml) of [Pd(1,5-C_8H_{12})Cl_2] (142.7 mg, 0.5 mmol) by adding $AgBF_4$ (194.7 mg, 1 mmol) and stirring for 3 h in the dark. The solution was filtered and cooled (255 K), dps (376.5 mg, 2 mmol) was added and the reaction mixture kept refrigerated for 2 d. At the end of this period, the solid was filtered, washed with diethyl ether and dissolved in boiling methanol. White crystals were obtained from this solution (final yield 70%). Analysis: calculated for $C_{20}H_{16}B_2F_8N_4PdS_2$: C 36.59, H 2.46, N 8.53, S 9.77%; found: C 36.6, H 2.6, N 8.5, S 9.8%. The analogous platinum compound, $[Pt(dps)_2](BF_4)_2$, was prepared in the same way (final yield 70%) and appeared to be isostructural with the Pd compound.

Crystal data

$[Pd(C_{10}H_8N_2S)_2](BF_4)_2$	Mo $K\alpha$ radiation
M_r = 656.5	λ = 0.71073 Å

Monoclinic
$P2_1/n$
$a = 7.603(1)$ Å
$b = 11.701(2)$ Å
$c = 14.434(2)$ Å
$\beta = 101.17(1)°$
$V = 1259.8(3)$ Å^3
$Z = 2$
$D_x = 1.731$ Mg m^{-3}
D_m not measured

Cell parameters from 25 reflections
$\theta = 8.0–16.4°$
$\mu = 0.979$ mm^{-1}
$T = 293$ K
Irregular
$0.30 \times 0.25 \times 0.19$ mm
Brown

Data collection

Siemens *R3m/v* diffractometer
$\omega/2\theta$ scans
Absorption correction:
  ψ scan (Kopfmann & Huber, 1968)
  $T_{min} = 0.5658$, $T_{max} = 0.6820$
4065 measured reflections
2897 independent reflections

2058 observed reflections $[F > 6\sigma(F)]$
$R_{int} = 0.0148$
$\theta_{max} = 27.5°$
$h = -1 \rightarrow 10$
$k = -1 \rightarrow 16$
$l = -19 \rightarrow 19$
3 standard reflections
  monitored every 97 reflections
  intensity decay: none

Refinement

Refinement on F
$R = 0.0272$
$wR = 0.0314$
$S = 1.48$
2058 reflections
197 parameters
H atoms: riding model, fixed isotropic U
$w = 1/[\sigma^2(F) + 0.0004F^2]$

$(\Delta/\sigma)_{max} = 0.095$
$\Delta\rho_{max} = 0.44$ e Å^{-3}
$\Delta\rho_{min} = -0.33$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.3.1)

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	0.03201 (8)
N1	0.0671 (3)	−0.1683 (2)	0.0070 (2)	0.0352 (7)
C1	0.0998 (4)	−0.2221 (3)	−0.0699 (2)	0.0395 (8)
C2	0.1560 (5)	−0.3346 (3)	−0.0671 (3)	0.053 (1)
C3	0.1789 (5)	−0.3930 (3)	0.0172 (3)	0.060 (1)
C4	0.1450 (5)	−0.3380 (3)	0.0960 (3)	0.056 (1)
C5	0.0901 (4)	−0.2257 (3)	0.0895 (2)	0.0450 (9)
S	0.0649 (1)	−0.14494 (7)	−0.17824 (6)	0.0497 (3)
C6	0.2245 (4)	−0.0364 (3)	−0.1423 (2)	0.0397 (9)
C7	0.3629 (5)	−0.0169 (3)	−0.1901 (2)	0.056 (1)
C8	0.4780 (5)	0.0726 (3)	−0.1631 (3)	0.065 (1)
C9	0.4573 (4)	0.1390 (3)	−0.0877 (3)	0.056 (1)
C10	0.3213 (4)	0.1149 (3)	−0.0412 (2)	0.044 (1)
N2	0.2046 (3)	0.0297 (2)	−0.0682 (2)	0.0362 (7)
B	0.8870 (6)	0.1539 (4)	0.6590 (3)	0.061 (1)
F1*a*‡	1.0493 (7)	0.1448 (9)	0.7143 (4)	0.149 (2)
F2*a*‡	0.8331 (9)	0.2669 (4)	0.6763 (3)	0.115 (2)
F3*a*‡	0.786 (1)	0.0828 (5)	0.7010 (5)	0.137 (2)
F1*b*§	0.997 (1)	0.0540 (8)	0.6650 (8)	0.135 (2)
F2*b*§	0.989 (2)	0.2329 (9)	0.6951 (7)	0.152 (2)
F3*b*§	0.740 (1)	0.128 (1)	0.6852 (8)	0.129 (2)
F4	0.8654 (5)	0.1493 (2)	0.5650 (2)	0.124 (1)

† Occupancy of 0.5. ‡ Occupancy of 0.6. § Occupancy of 0.4.

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

Pd—N1	2.032 (2)	C4—C5	1.377 (5)
Pd—N2	2.026 (3)	S—C6	1.764 (3)
N1—C1	1.341 (4)	C6—C7	1.384 (5)
N1—C5	1.349 (4)	C6—N2	1.351 (4)
C1—C2	1.383 (4)	C7—C8	1.372 (5)
C1—S	1.780 (3)	C8—C9	1.370 (6)
C2—C3	1.376 (5)	C9—C10	1.367 (5)
C3—C4	1.375 (6)	C10—N2	1.341 (4)
N1—Pd—N2	88.93 (9)	C1—S—C6	97.5 (1)
N1—Pd—N2^i	91.07 (9)	S—C6—N2	118.0 (2)
N1—C1—S	118.0 (2)	S—C6—C7	121.2 (3)
N1—C1—C2	121.9 (3)	C7—C6—N2	120.8 (3)
C2—C1—S	120.1 (2)	C6—C7—C8	119.2 (3)
C1—C2—C3	119.0 (3)	C7—C8—C9	119.6 (4)
C2—C3—C4	119.2 (4)	C8—C9—C10	119.2 (3)
C3—C4—C5	119.5 (3)	C9—C10—N2	122.1 (3)
N1—C5—C4	121.4 (3)	C6—N2—C10	119.1 (3)

Symmetry code: (i) $-x, -y, -z$.

The crystal structure of the title compound was determined by single-crystal X-ray diffraction using a Siemens automated four-circle *R3m/V* diffractometer with the corresponding *SHELXTL-Plus* package (Sheldrick, 1992) implemented on a MicroVAX 3400 computer. Geometric calculations were performed using a locally modified version of *PARST* (Nardelli, 1995). Reflection intensities were evaluated by profile fitting of a 96-step peak scan among 2θ shells (Diamond, 1969) and then corrected for Lorentz-polarization effects. Standard deviations $\sigma(I)$ were estimated from counting statistics. An absorption correction was applied by fitting a pseudo-ellipsoid to the azimuthal scan data (0–360° range by a 10° step) of 13 high χ reflections (Kopfmann & Huber, 1968). The model of the structure, solved by the Patterson method and completed by a combination of least-square techniques and difference Fourier synthesis, was refined by full-matrix least-square minimization of $\Sigma w(F_o - F_c)^2$. The refinement was hindered by the rotational disorder of the BF_4^- anion which was split into two staggered orientations rotated with respect to the B—F4 bond axis.

Data collection: *P3/V* (Siemens, 1989). Cell refinement: *P3/V*. Data reduction: *SHELXTL-Plus*. Program(s) used to refine structure: *SHELXTL-Plus*. Molecular graphics: *XP* in *SHELXTL-Plus*. Software used to prepare material for publication: *SHELXTL-Plus* and *PARST*.

Financial support for this work was provided by MURST of Italy.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1236). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). C**52**, 2191–2193

Bis(nitrato-*O*,*O*′)bis{2-[2-(2-thienyl)-ethynyl]pyridine-*N*}cobalt(II)

HUUB KOOIJMAN,[a]* ANTHONY L. SPEK,[a] THOMAS X. NEENAN[b]† AND WILLEM L. DRIESSEN[b]

[a]*Bijvoet Center for Biomolecular Research, Department of Crystal and Structural Chemistry, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands, and* [b]*The Leiden Institute of Chemistry, Gorlaeus Laboratories, Leiden University, PO Box 9502, 2300 RA Leiden, The Netherlands. E-mail: huub@chem.ruu.nl*

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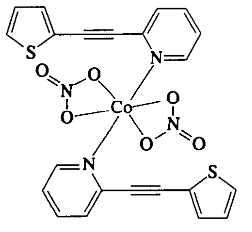
Abstract

The title compound, $[\mathrm{Co(NO_3)_2(C_{11}H_7NS)_2}]$, has twofold axial symmetry. The central cobalt ion is coordinated by four O atoms of two nitrate anions and two N atoms of two 2-[2-(2-thienyl)ethynyl]pyridine ligands in a distorted octahedral geometry. The non-coordinating thiophene moiety is disordered over two overlapping orientations. Short bifurcated C—H···O interactions link the molecules into an infinite chain parallel to the *c* axis.

Comment

The structure of the 1-(2-pyridyl)-2-(2-thienyl)ethyne–cobalt complex, (I), was investigated as part of a study on new modes of coordination of ligands connected by rigid groups such as acetylenes (Neenan & Driessen, 1996; Neenan, Driessen, Haasnoot & Reedijk, 1996).



(I)

The cobalt ion in (I) is coordinated by two nitrate ions and two pyridyl N atoms and is located on a crystallographic twofold rotation axis. The triple bond of the acetylene moiety and the thiophene S atom do not participate in the coordination. The coordination sphere of cobalt is octahedral, with a severe distortion due to the small bite angle of the nitrate anions. Although nitrate ions do not often coordinate with cobalt, nine $\mathrm{Co(NO_3)_2}$ fragments out of 83 structures containing both cobalt(II) and at least one nitrate ion are reported in the Cambridge Structural Database (Allen & Kennard, 1993). All of these display the nitrate ions in the '*cis*' orientation observed in the present structure. The observed distances in the coordination sphere of the Co atom are in agreement with the values reported in the literature. Uneven Co—O bond lengths have been reported for other complexes and are often associated with a strong distortion of the octahedral geometry towards a tetrahedral one (*e.g.* Han & Parkin, 1991). Each pyridine ring is virtually coplanar with one nitrate anion, as is indicated by the angle between the least-squares planes of 3.3 (3)°. The angle between the least-squares planes through the thiophene and pyridine rings (in the same ligand molecule) is 6.1 (8)°. A view of (I) is shown in Fig. 1.

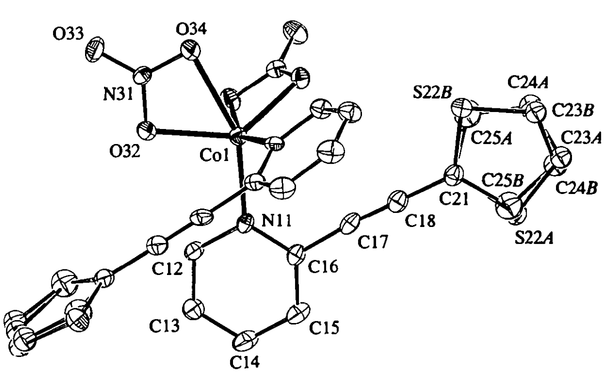


Fig. 1. Atomic displacement parameter plot (30% probability level) of the title compound, with the atomic labelling scheme, showing the disorder in the thiophene ring. Labels with suffix *A* denote the major disorder component.

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† Senior Visiting Fellow 1994. Permanent address: AT&T Bell Laboratories, Murray Hill, NJ 07974, USA.