

angles between the plane of the three S atoms and the plane of each thiophene ring are 91.4, 88.7 and 93.7°, respectively, as compared with 123.4, 124.4 and 119.7° in the complex. Bond distances and angles within the thiophene group of the title species, e.g. C—S 1.689 (5)–1.722 (4) Å, C—S—C 91.0 (2)–92.4 (3)°, are similar to those in the free S₃tren molecule.

The I₃ anion has I—I bond distances of 2.8610 (5) and 2.9729 (4) Å; the mean I—I distance in six I₃⁻ ions is 2.9717 (11) Å (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987). The I—I—I angle is 178.13 (1)°. The chloroform solvate possesses no unusual features.

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Structure of *trans*-Dibromobis(5,7-dimethyl-8*H*-[1,2,4]triazolo[1,5-*a*]pyrimidine)-palladium(II) Methanol Solvate

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Abstract. [PdBr₂(C₇H₈N₄)₂].CH₃OH, *M*_r = 594.58, triclinic, *P* $\bar{1}$, *a* = 9.153 (4), *b* = 8.858 (5), *c* = 8.317 (3) Å, α = 123.54 (3), β = 92.25 (3), γ = 109.31 (3)°, *V* = 508.9 Å³, *Z* = 1, *D*_x = 1.94, *D*_m = 1.93 Mg m⁻³, λ (Mo *K*α) = 0.71073 Å, μ = 4.811 mm⁻¹, *F*(000) = 288.0, *T* = 293 K, *R* = 0.035 for 1474 unique reflections [*I* > 2σ(*I*)]. The two triazolopyrimidine ligands are coordinated to palladium *via* N(3) at a distance of 2.015 (4) Å; the bromides are *trans* coordinated at a distance of 2.4196 (7) Å, which is in the range expected for this type of complex.

Introduction. Square-planar palladium and platinum compounds are of interest in inorganic and organometallic chemistry. For example, the antitumour activity of *cis*-Pt(NH₃)₂Cl₂ and related compounds has been studied extensively. It is observed that the platinum ion binds preferentially *via* N(7) of the guanine base in DNA (Reedijk, Fichtinger-Schepman, van Oosterom & van der Putte, 1987).

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Triazolopyrimidines are of interest because of their use as models for naturally occurring purines. Recently a systematic study concerning the coordination compounds of dimethyltriazolopyrimidine (dmtp) has been started in our laboratory (Favre, Haasnoot & Reedijk, 1986; Biangini-Cingi, Manotti-Lanfredi, Tiripicchio, Haasnoot & Reedijk, 1983; Dillen, Lenstra, Haasnoot & Reedijk, 1983). Previous crystal structure determinations of metal compounds containing dmtp ligands have revealed that binding occurs only *via* N(3) of the ligand. We now investigate whether the same nitrogen atom coordinates to palladium, and compare this system with previously reported, related palladium compounds.

Experimental. Yellow crystals of [PdBr₂(C₇H₈N₄)₂].CH₃OH were obtained after refluxing PdBr₂ and dmtp (1:4) in methanol (60 mL) for 3 h. A rod-shaped single crystal was selected for the crystal structure determination. Experimental data for the compound are shown in Table 1. Analysis: Calculated for C₁₅H₂₀Br₂N₈OPd: C 30.30, H 3.39, N 18.85, O 2.69%; found C 30.56, H 3.34, N 18.80, © 1990 International Union of Crystallography

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Table 1. Experimental data for [PdBr₂(dmp)₂]-CH₃OH

Diffractometer	Enraf-Nonius CAD-4
Temperature (K)	293
Scan method	$\theta/2\omega$
Quadrants	$\pm h, \pm k, l$
θ range (°)	2–30
Standard reflections	$\bar{3}20$
(variation within 10%)	320
No. of reflections measured	3452
No. of independent reflections	2974
R_{int}	0.03
No. of significant reflections [$I > 2\sigma(I)$]	1474
h	–12 to 12
k	–12 to 12
l	0 to 11
Crystal size (mm)	0.2 × 0.1 × 0.1
Transmission factor range	0.72–0.84
$\Delta\rho_{max}$ (e Å ⁻³)	2.3
$\Delta\rho_{min}$ (e Å ⁻³)	–2.3
R	0.034
wR	0.037
Weighting scheme	1/ $\sigma^2(F)$
(Δ/σ) _{max}	0.097
S (goodness of fit)	1.67

Table 2. Fractional atomic coordinates [$\times 10^3$ for C(10) and O(1), $\times 10^4$ for the rest] and isotropic thermal parameters [$\times 10^2$ for Pd, Br, N(3), N(4) and N(8), $\times 10$ for the rest] of trans-[PdBr₂(C₇H₈N₄)₂].CH₃OH

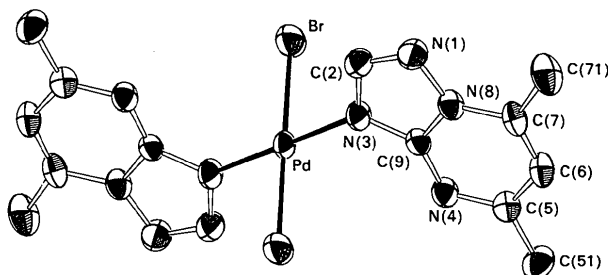
$$B_{iso} = \frac{3}{2}\pi^2 \text{trace}(U).$$

	x	y	z	$B_{iso}(\text{\AA}^2)$
Pd	0	0	0	254 (2)
Br(1)	534 (1)	–46 (1)	–2848 (1)	404 (2)
N(1)	4639 (5)	971 (7)	2294 (7)	34 (2)
C(2)	3058 (7)	45 (9)	1549 (10)	35 (2)
N(3)	2369 (4)	985 (7)	1172 (7)	295 (15)
N(4)	3566 (5)	4213 (7)	1826 (7)	279 (14)
N(8)	4975 (4)	2687 (7)	2448 (7)	266 (14)
C(5)	4990 (7)	5766 (8)	2568 (8)	30 (2)
C(6)	6449 (7)	5781 (8)	3239 (8)	32 (2)
C(7)	6458 (7)	4258 (8)	3211 (8)	31 (2)
C(9)	3583 (5)	2708 (8)	1788 (7)	252 (15)
C(51)	5001 (8)	7497 (8)	2675 (10)	39 (2)
C(71)	7888 (7)	4113 (9)	3935 (10)	43 (2)
O(1)	–19 (3)	492 (4)	–80 (3)	149 (7)
C(10)	122 (2)	536 (2)	1004 (3)	73 (8)

O 2.86%. D_m was determined by flotation. X-ray intensity data were collected by using graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Cell constants were determined from setting angles of 24 reflections (θ between 10 and 12°). Lorentz, polarization and absorption corrections were performed with local program systems. The structure was solved by standard Patterson techniques and refined using full-matrix least squares based on F with weights $w = 1/\sigma_F^2$. The non-hydrogen atoms were refined anisotropically. The palladium atom lies on a special position at (0,0,0). Hydrogen atoms were placed in calculated positions at 1.0 Å from the adjacent non-hydrogen atoms and were refined isotropically coupled with the adjacent carbon atoms. A

Table 3. Bond distances (Å) and bond angles (°) of trans-[PdBr₂(C₇H₈N₄)₂].CH₃OH

Pd–Br(1)	2.4196 (7)	C(5)–C(6)	1.420 (8)
Pd–N(3)	2.015 (4)	C(6)–C(7)	1.338 (7)
N(1)–C(2)	1.317 (7)	C(7)–N(8)	1.375 (7)
C(2)–N(3)	1.345 (7)	N(8)–C(9)	1.377 (6)
N(3)–C(9)	1.340 (6)	C(5)–C(51)	1.483 (8)
C(9)–N(4)	1.321 (7)	C(7)–C(71)	1.493 (8)
N(4)–C(5)	1.336 (7)	N(1)–N(8)	1.377 (6)
Br(1)–Pd–N(3)	90.6 (1)	N(8)–C(7)–C(6)	115.3 (5)
C(2)–N(1)–N(8)	101.7 (4)	C(5)–C(6)–C(7)	121.5 (5)
N(1)–C(2)–N(3)	115.4 (5)	N(4)–C(5)–C(6)	121.9 (5)
C(2)–N(3)–C(9)	105.3 (5)	N(4)–C(5)–C(51)	117.5 (5)
N(3)–C(9)–N(8)	106.5 (5)	C(6)–C(7)–C(71)	127.0 (5)
C(7)–N(8)–C(9)	121.8 (5)		

Fig. 1. The structure of [PdBr₂(C₇H₈N₄)₂].CH₃OH. Thermal ellipsoids are shown at 50% probability. The methanol molecule and hydrogen atoms have been omitted for reasons of clarity.

molecule of methanol was found, which was disordered about two equally populated positions. In effect, apart from the solvent inclusion, the structure refined very well in the centrosymmetric space group $P\bar{1}$. Attempts to refine the structure in $P1$ did not yield any improvement in the definition of the solvent molecule. Some residual peaks are present in the final difference Fourier map due to disorder. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). The programs used were written or modified by Mrs E. W. Rutten-Keulemans and R. A. G. de Graaff.

Discussion. Atom coordinates and equivalent isotropic thermal parameters for the non-hydrogen atoms are shown in Table 2. Fig. 1 shows a projection of the molecule with the atomic numbering scheme. Relevant bond distances and bond angles are presented in Table 3.* Fig. 1 shows that the coordination mode of the triazolopyrimidine is via N(3), as in other triazolopyrimidine complexes (Favre, Haasnoot & Reedijk, 1986; Biagini-Cingi, Manotti-Lanfredi, Tiripicchio, Haasnoot & Reedijk,

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53188 (9 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

1983; Dillen, Lenstra, Haasnoot & Reedijk, 1983). The Pd—N(3) distance of 2.014 (4) Å and the Pd—Br distance of 2.4196 (7) Å are normal by comparison with *trans*-Pd[2-(2'-thienyl)pyridine]₂Br₂ (Giordano, Butler & Rasmussen, 1978). Two other related structures are *trans*-Pd(L)₂Cl₂ (L = 1-methylimidazole and 2-methylimidazole), for which metal–nitrogen distances of 2.011 (4) and 2.005 (3) Å were found (Navarro-Ranninger, Martinez-Carrera & Garcia-Blanco, 1983*a,b*). The shortest Br—Br contact observed in the structure is 3.727 (1) Å. No hydrogen bonds between the methanol molecules and the bromine atoms were found. This agrees with the observed ν_{OH} of MeOH of 3520 cm⁻¹. The shortest intramolecular distance found is that between N(4) and H(11) with a distance of 2.61 (2) Å. Molecular packing is therefore dictated solely by van der Waals forces.

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The Structure of Dilithium Dihydrogen 1,2,4,5-Benzenetetracarboxylate Tetrahydrate (Dilithium Dihydrogen Pyromellitate Tetrahydrate)

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Abstract. Li₂C₁₀H₄O₈·4H₂O, *M_r* = 338.1, triclinic, *P* $\bar{1}$, *a* = 4.586 (1), *b* = 8.539 (4), *c* = 8.525 (3) Å, α = 87.66 (5), β = 89.21 (3), γ = 89.80 (2)°, *V* = 333.5 (4) Å³, *Z* = 1, *D_x* = 1.683 Mg m⁻³, $\lambda(\text{Mo K}\alpha)$ = 0.71069 Å, μ = 0.15 mm⁻¹, *F*(000) = 172, room temperature, *wR* = 0.034 for 1204 reflections [*I* > 2 σ (*I*)]. The pyromellitate anions are located at centers of symmetry and are stacked along [100]. They form (11 $\bar{1}$) layers *via* two strong intermolecular hydrogen bonds (2.46 and 2.50 Å) which extend across centers of symmetry. These layers are connected by Li ions which have approximate tetrahedral coordination (two carboxylic O atoms and two H₂O molecules).

Introduction. Recent IR spectroscopic investigations of several acid salts of pyromellitic acid (Luehrs, Cornilsen, Glover & Neils, 1988) suggested the presence of strong hydrogen bonds. Only a few of these salts have been characterized by crystal structure analysis so far. One of these, an acid Co-pyromellitate, has a very short intramolecular

hydrogen bond (Ward & Luehrs, 1983). Since several lithium salts of phthalic acid were found to have very short intramolecular hydrogen bonds (Gonschorek & Küppers, 1975; Adiwidjaja & Küppers, 1978; Küppers, Takusagawa & Koetzle, 1985), lithium was chosen as cation in the present study in order to find another example of a compound with a short intramolecular hydrogen bond.

Experimental. Single crystals were grown from an aqueous solution of a stoichiometric mixture of LiOH·H₂O (Fluka, p.a.) and pyromellitic acid (Fluka, recrystallized) by slow evaporation. Optical microscopy indicated that two phases were present: (1) many poorly crystallized needles and (2) a few prismatic crystals of good quality. One of these (0.1 × 0.2 × 0.2 mm) was mounted on a Siemens–Stoe AED2 diffractometer and 2091 intensities were collected (θ range 2–30°, θ –2 θ mode, 153 reflections rejected as unobserved, 1627 unique, *R*_{int} = 0.015). Index ranges were *h* – 6/6, *k* – 12/12, *l* 0/12. Three standard reflections monitored every 60 min