constrained geometry (*DFIX* parameter in *SHELX*76: N—H = 1.01 Å). Considering the values of $\Delta\rho_{max}$ and $\Delta\rho_{min}$ no attempt was made to refine the H-atom positional parameters.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55553 (20 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: DU1021]

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Structure of Potassium Theobrominium Tetrakis(thiocyanato)palladate(II) Monohydrate

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Abstract

The main structural features are columns of alternating theobrominium cations, protonated at N(9), and tetrakis(thiocyanato)palladate(II) anions. The anions are in the shape of a gammadion, with small but significant deviations from C_{4h} symmetry. Average stereochemical data for the $[Pd(SCN)_4]^{2-}$ anion are given.

Comment

Potassium theobrominium tetrakis(thiocyanato)palladate(II) monohydrate was prepared in the course of our research into the metal complexes of purine bases (Colacio *et al.*, 1989, and references therein; Skipworth *et al.*, 1992). Although there is no bond between the Pd atom and the base in this structure, it has some interesting features.

The tetrakis(thiocyanato)palladate(II) anions are in the shape of a gammadion,* but with some significant deviations from C_{4h} symmetry (Fig. 1). The thiocyanato ligands are linear and the four S atoms are coplanar to within experimental error, with the Pd atom displaced by 0.013(1) Å from the S_4 least-squares plane. The thiocyanato ligands (1′, 2′, 3′, 4′) lie at angles of 88.48(4), 76.22(4), 89.08(4) and 84.26(4)°, respectively, to the normals to this plane. Average stereochemical data for the anion are: Pd—S 2.338(1), S—C 1.673(5), C—N, 1.138(6) Å and Pd—S—C 107.6(2)°. A search of the literature, including the Cambridge Structural Database (Allen *et al.*, 1991), revealed only one other example of the $[Pd(SCN)_4]^{2-}$ anion [in $K_2Pd(SCN)_4$ (Mawby & Pringle, 1972), a structure that was determined from limited film data]. The details of the $[Pd(SCN)_4]^{2-}$ anion reported here therefore represent the best available stereochemical data for this anion. There is an example of the $[Pt(SCN)_4]^{2-}$ analogue (Gysling & Luss, 1984), but the anion is disordered.

The theobrominium cations are protonated at N9. The C8—N7 and C8—N9 bond lengths are not significantly

* A gammadion is a pattern formed of combinations of the Greek letter gamma and is suggested here as a name to cover all species of this shape.

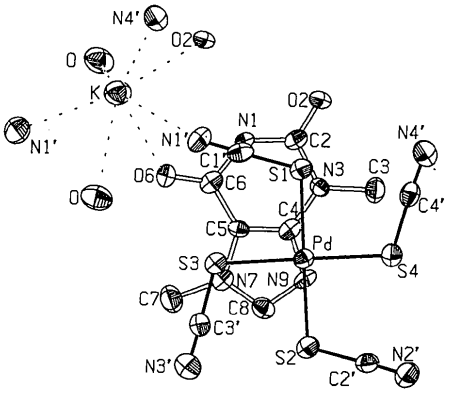

Fig. 1. The complex cation and anion viewed perpendicular to their planes and including the environment of the potassium ion. Thermal ellipsoids are represented at the 50% probability level and H atoms are omitted for clarity.

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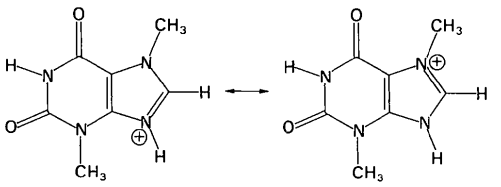
different indicating that, in so far as the five-membered rings are concerned, the following structures contribute equally to the resonance hybrid. Other distances and angles are unremarkable.



The main structural features in the crystal are columns composed of alternate theobrominium cations and complex anions. The column axes lie parallel to *b* and both planar species are tilted at about 13° to [010] so that the perpendicular separations of anion and cation are approximately 3.52 and 3.48 Å.

Hydrogen bonds between N1 and O2 of adjacent theobrominium cations [N1···O2 at 2 $-x$, $-y$, $1-z$; 2.850(8) Å] around a centre of symmetry link these same columns in pairs (Fig. 2). Two tetrakis(thiocyanato)palladate(II) anions in the same columns are related by a centre of symmetry *b*/2 away. Potassium ions and water molecules are situated in channels between two of these pairs of columns stacked side by side. The potassium ion is in an irregular sevenfold coordination while the water molecule has two interactions with potassium ions [2.837(6), 2.857(6) Å] and several possible H-bonded contacts to O atoms in the base. A short hydrogen bond [N9···N2′ at 1 $-x$, $1-y$, $1-z$] of 2.74(1) Å is a sufficiently strong interaction to displace N2′ from the otherwise nearly planar complex anion as is shown by the thiocyanate-to-S_4 plane angles given above.

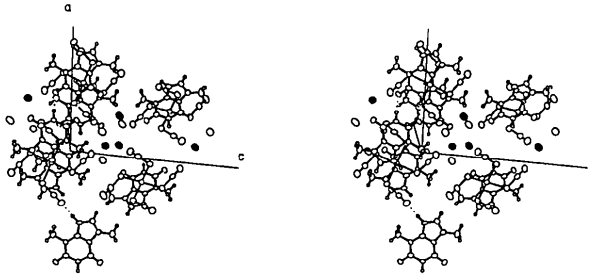


Fig. 2. A view of part of the crystal structure showing columns of alternate cations and anions surrounding a channel of water molecules and potassium ions; the positive **b** direction is towards the viewer. Potassium ions are are represented by closed circles and hydrogen bonds by dashed lines.

Experimental

Crystal data

$C_7H_9N_4O_2^+.C_4N_4PdS_4^{2-}.H_2O.K^+$
M_r = 576.998
Monoclinic
$P2_1/c$
a = 15.172 (2) Å
b = 7.1730 (8) Å
c = 18.619 (1) Å
β = 95.980 (7)°
V = 2015.3 (4) Å^3
Z = 4
D_x = 1.902 Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 25 reflections
θ = 3–13°
μ = 1.544 mm^{-1}
T = 293 K
Needle
0.650 × 0.058 × 0.024 mm
Red

Data collection

Enraf–Nonius CAD-4 diffractometer
ω/θ scans
Absorption correction: Gaussian
T_{min} = 0.9160, T_{max} = 0.9644
3750 measured reflections
1557 independent reflections
1510 observed reflections [$F^2>0$]
R_{int} = 0.027
θ_{max} = 20°
h = −14 → 14
k = 0 → 6
l = −17 → 17
2 standard reflections
frequency: 120 min
intensity variation: none

Refinement

Refinement on F
Final R = 0.034
wR = 0.029
S = 1.763
1510 reflections
253 parameters
H-atom parameters not refined
Weighting scheme based on measured e.s.d.'s
$(\Delta/\sigma)_{max}$ = 0.004
$\Delta\rho_{max}$ = 0.425 e Å^{-3}
$\Delta\rho_{min}$ = −0.472 e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

Data reduction: *FLUCAD* (Taylor, 1980); *Xtal ADDREF*, *ABSORB* and *SORTRF* (Hall & Stewart, 1990). Program(s) used to solve structure: *Xtal FOURR*, *FC*, *MODEL*, *PEKPIK* and *ADDATM*. Program(s) used to refine structure: *Xtal CRYLSQ*, *BONDAT*, *CONTRS*, *PLOTX* and *SLANT*. Molecular graphics: *Xtal ORTEP*. Software used to prepare material for publication: *Xtal BONDLA*, *LSQPL* and *LISTFC*.

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal 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	0.71102 (4)	0.55862 (9)	0.41507 (4)	0.0278 (4)
K	1.0601 (1)	0.1163 (3)	0.2891 (1)	0.049 (1)
O	0.9096 (4)	0.2247 (8)	0.1950 (3)	0.055 (4)
S1	0.8575 (1)	0.5174 (3)	0.4658 (1)	0.038 (1)
C1′	0.9171 (5)	0.456 (1)	0.3985 (5)	0.037 (5)
N1′	0.9591 (5)	0.412 (1)	0.3538 (4)	0.058 (5)
S2	0.5636 (1)	0.5953 (3)	0.3666 (1)	0.046 (1)
C2′	0.5105 (5)	0.703 (1)	0.4293 (4)	0.034 (5)
N2′	0.4732 (5)	0.778 (1)	0.4704 (4)	0.050 (5)
S3	0.7508 (1)	0.4881 (3)	0.2999 (1)	0.039 (1)
C3′	0.6584 (6)	0.497 (1)	0.2422 (5)	0.044 (6)
N3′	0.5973 (5)	0.501 (1)	0.2020 (4)	0.073 (6)
S4	0.6690 (1)	0.6281 (3)	0.5290 (1)	0.041 (1)
C4′	0.7593 (5)	0.640 (1)	0.5876 (4)	0.035 (5)
N4′	0.8188 (5)	0.653 (1)	0.6305 (4)	0.059 (5)
N1	0.8940 (4)	−0.0006 (8)	0.4366 (3)	0.030 (4)
C2	0.8670 (5)	0.034 (1)	0.5031 (5)	0.029 (5)
O2	0.9184 (3)	0.0390 (8)	0.5577 (3)	0.039 (4)
N3	0.7767 (4)	0.0668 (9)	0.5051 (3)	0.026 (4)
C3	0.7421 (5)	0.115 (1)	0.5737 (4)	0.039 (5)

C4	0.7244 (5)	0.062 (1)	0.4417 (4)	0.028 (5)
C5	0.7534 (5)	0.021 (1)	0.3765 (4)	0.026 (5)
C6	0.8442 (5)	−0.012 (1)	0.3692 (5)	0.030 (6)
O6	0.8802 (3)	−0.0422 (8)	0.3146 (3)	0.041 (4)
N7	0.6784 (4)	0.0300 (9)	0.3254 (3)	0.034 (4)
C7	0.6752 (6)	−0.004 (1)	0.2478 (5)	0.050 (6)
C8	0.6100 (5)	0.071 (1)	0.3601 (5)	0.035 (5)
N9	0.6348 (4)	0.0918 (8)	0.4313 (3)	0.030 (4)

Table 2. *Geometric parameters* (Å, °)

Pd—S1	2.341 (2)	N1—C6	1.40 (1)
Pd—S2	2.338 (2)	C2—O2	1.217 (9)
Pd—S3	2.343 (2)	C2—N3	1.39 (1)
Pd—S4	2.331 (2)	N3—C4	1.352 (9)
S1—C1′	1.680 (9)	N3—C3	1.47 (1)
C1′—N1′	1.14 (1)	C4—C5	1.36 (1)
S2—C2′	1.675 (9)	C4—N9	1.371 (9)
C2′—N2′	1.13 (1)	C5—N7	1.407 (9)
S3—C3′	1.677 (9)	C5—C6	1.42 (1)
C3′—N3′	1.13 (1)	C6—O6	1.22 (1)
S4—C4′	1.662 (8)	N7—C8	1.31 (1)
C4′—N4′	1.14 (1)	N7—C7	1.46 (1)
N1—C2	1.37 (1)	C8—N9	1.35 (1)
S4—Pd—S2	89.22 (8)	C4—N3—C2	117.4 (7)
S4—Pd—S1	89.85 (8)	C4—N3—C3	122.2 (6)
S4—Pd—S3	179.08 (6)	C2—N3—C3	120.2 (6)
S2—Pd—S1	178.6 (1)	N3—C4—C5	124.6 (7)
S2—Pd—S3	89.89 (8)	N3—C4—N9	127.1 (7)
S1—Pd—S3	91.03 (8)	C5—C4—N9	108.3 (6)
C1′—S1—Pd	107.1 (3)	C4—C5—N7	106.2 (6)
N1′—C1′—S1	178.3 (8)	C4—C5—C6	121.8 (7)
C2′—S2—Pd	107.0 (3)	N7—C5—C6	131.9 (7)
N2′—C2′—S2	178.2 (7)	O6—C6—N1	120.7 (7)
C3′—S3—Pd	107.5 (3)	O6—C6—C5	129.2 (7)
N3′—C3′—S3	178.3 (9)	N1—C6—C5	110.1 (7)
C4′—S4—Pd	108.9 (3)	C8—N7—C5	107.6 (6)
N4′—C4′—S4	176.3 (8)	C8—N7—C7	125.3 (7)
C2—N1—C6	129.7 (6)	C5—N7—C7	127.1 (7)
O2—C2—N1	122.4 (7)	N7—C8—N9	110.8 (7)
O2—C2—N3	121.3 (8)	C8—N9—C4	107.0 (7)
N1—C2—N3	116.3 (7)		

The compound was prepared by the Spanish authors by the reaction of an aqueous solution (10 ml) of K_2PdCl_4 (0.33 g, 1 mmol) and KSCN (0.97 g, 10 mmol) with a suspension of theobromine (2 mmol) in 100 ml of ethanol under reflux for 1 h. The resulting red solution was allowed to stand at room temperature for three days, whereupon crystals of the complex formed. These were filtered off and dried with diethyl ether.

The structure was solved by a combination of Patterson and Fourier methods. Positions of all H atoms, except for those of the water molecule, were observed in difference maps but they were placed at calculated positions. Two cycles of refinement including an extinction parameter resulted in an extinction coefficient not significantly different from zero. These refinement cycles were discarded.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55780 (17 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HL1021]

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Structure of Tetracarbonyl[*N*,*N*,*N*′,*N*′-tetramethylethylenediamine-*N*,*N*′]-molybdenum(0)

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Abstract

The tetramethylethylenediamine ligand is bidentate to the Mo atom to give a distorted octahedral environment. The average Mo—C, Mo—N, N—C

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