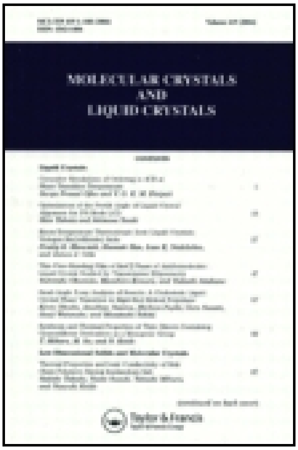

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Interstack Interactions in Potassium Bis(1,2-Cyclobutenedione 3,4-dithiolato) Palladate. Crystal Structure

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Potassium bis(1,2-cyclobutenedione 3,4-dithiolato) palladate (Pd(dithiosquarato)$_2$K$_2$) crystallizes in the monoclinic system, space group $P2_1/c$, a = 8.046(2), b = 15.235(4), c = 6.289(1). The dithiosquarate entities are stacked in parallel columns separated by potassium cations and water molecules. π-interactions within a stack are evidenced by the short stacking distance (3.51 Å). Further interstack interactions involve close S. . .O or O. . .O interstack contacts. (~3.5 Å). As a result, the structural arrangement is nearly two-dimensional. Conductivity measurements carried out on pressed pellets show a semi-conductive behavior ($\sigma = 2 \times 10^{-5}\ \Omega^{-1}\ \text{cm}^{1}$).

Keywords: bidimensional, dithiosquaric acid, semi-conductive properties.

INTRODUCTION

Low-dimensional materials of molecular inorganic complexes building units have attracted considerable attention in the past years. Planar complexes, particularly those containing d^8 metal ions, can form structures with linear chains of heavy metal atoms and short metal-metal distances. Bond strengths within such chains may eventually be increased by partial oxidation, resulting in high anisotropic metallic behavior giving rise to unusual physical and chemical properties for these compounds.[1]

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The tetracyanoplatinate system is one of the most important examples of such compounds,[2] but it was shown that the use of unsaturated sulphur donor ligands such as dithiolene may also favor partial or unusual oxidation states and thus lead to organometallic polymers offering 1D properties.[3] We report in this paper a study of palladium metal complexes using dithiosquaric acid as sulphur donor ligand. 1,2-cyclo-butenedione-3,4-dithiolate (the dianion of the cis-dithiosquaric acid: $(dtsq)^{2-}$) is an attractive ligand since it consists of a quasi planar molecule associated with a conjugated ring system. Such properties may be used for building stacked structures and lead to fractional oxidation states. Molecular architectures related to those observed in oxalatoplatinates[4] or in the dithiolene complexes[3] should be expected. Some transition metal complexes of dithiosquaric acid were previously characterized by Coucouvanis *et al.*[5] While platinum and nickel complexes appear to have the usual characteristics for such compounds, the palladium analogues exhibit a shiny green color, which remains unchanged in solution. This led us to initiate the X-ray structural determination and the physicochemical study of these compounds.

EXPERIMENTAL

Preparation.—The chemicals were used as purchased. 1.2 potassium dithiosquarate was prepared from diethylsquarate. An ethanolic solution of diethyl squarate was added to a KHS suspension upon stirring for 3 h. The yellow precipitate formed was recrystallized from hot water. Diethyl squarate was prepared by refluxing perchlorocyclobutezone in absolute ethanol.[6]

Potassium Bis Dithiosquarato Palladate (*II*).—A solution of K_2PdCl_4 (10^{-3} mol) in the minimum amount of water is slowly added to potassium dithiosquarate (2×10^{-3} mol) dissolved in 20 ml of water. The solution soon turned green. It was cooled for a few hours, after which green glittering crystals with pronounced metallic luster separated. Chemical Analysis. Found % (Calculated %) for $K_2[Pd(C_4O_2S_2)_2]_2$, $2H_2O$: C, 19.07 (18.89); H, 0.68 (0.78); Pd, 20.48 (20.86).

Barium Bis Dithiosquarato Palladate(*II*) *and Bis* (*tetraphenylphosphonium*) *Bis Dithiosquarato Palladate*(*II*) are prepared as described in the literature.[5] Chemical Analysis. Found % (Calculated %) for Ba $[Pd(C_4O_2S_2)_2]$, $4H_2O$: C, 15.26 (15.91); H, 1.42 (1.32); Pd, 17.69 (17.57). Found % (Calculated %) for $(P(C_6H_5)_4)_2[Pd(C_4O_2S_2)_2]$: C, 62.43 (62.68); H, 3.41 (3.73).

Physical Measurements.—Electronic spectra were recorded on a Cary-14 spectrophotometer in the 800–200 nm range.

E.s.r. spectra were obtained with a Bruker ER.200K with a conventional X-band (9.6 GHz). The microwave frequency was calibrated with diphenylpicrylhydrazyl. All e.s.r. spectra were recorded on frozen aqueous solutions directly on the mother solution, they were also recorded on a powdered sample in a large range of temperature.

Magnetic susceptibilities were determined by the Faraday method using a Sartorius microbalance coupled with a Drusch electromagnet. The measurements have been performed between 80 and 320 K. $HgCo(SCN)_4$ was used as standard ($\chi_g = (16.44 \times 10^{-6})$ uem cgs). A small amount of ferro-magnetism was found in the samples upon variation of the applied field at various temperatures. Magnetic susceptibility data were corrected for this ferromagnetism by extrapolation to infinite field. The experimental values were corrected for the diamagnetism of the ligand.

Powder conductivities were determined on compressed pellets with a Wayne Kerr automatic component Bridge B 605. The pellets were pressed and their resistance directly measured in a "conductivity press" by applying a force of 100 Kg on 3 mm diameter pistons moving in a glass capillary tube.[7]

Collection and Reduction of X-ray Data.—$K_2Pd(C_4O_2S_2).2H_2O$. The crystal used for structure determination was shapeless. To avoid problems connected with its low stability the crystal was sealed in a Lindemann glass capillary containing the mother liquor. Pertinent details for data collection and reduction procedures are given in Table I.

Structure Solution and Refinement.—The structure was determined by the heavy-atom method. A Patterson map revealed the position of the palladium atom. All other atoms but hydrogen were located by the usual combination of Fourier and least square calculations. The water hydrogen atoms were not located from a difference electron density map. Neutral-atom scattering factors for non-hydrogen atoms and corrections for anomalous dispersion terms for palladium were taken from usual sources.[8]

The final full-matrix least-squares refinement converged to $R_{(F)}$ and $Rw_{(F)}$ factors of 0.041 and 0.059. The weighting scheme used in the minimization of the function $\Sigma w(|Fo|-|Fc|)^2$ is defined as $w = (\sigma^2(Fo) + (pFo)^2)^{-1}$, where p is the factor to prevent overweighting of strong reflections (fixed here to 0.03). The final difference Fourier was featureless.

TABLE I

Summary of crystal data and intensity collection

compd	$K_2Pd(C_4O_2S_2)_2$, $2H_2O$
formula	$C_8H_4K_2O_6PdS_4$
a (at 20°C)	8.046 (2) Å
b	15.235 (4) Å
c	6.289 (1) Å
β	93.95
V	769 Å^3
Z	2
ρcal	1.987 g cm^3
cryst syst.	Monoclinic
space group	C_{2h}^5-$P2_1/c$
crystal volume approximately	0.7 mm^3
temp	20°C
radiation	Mo Kα from monochromator (λ MoKα = 0.71069)
linear absorption coefficient	14.24 cm^{-1}
instrument	CAD4 diffractometer from NONIUS
take-off angle	4.5°
scan mode	ω/2θ
scan speed	4° in θ/min
scan range	0.5° below $K\alpha_1$ above $K\alpha_2$
2θ limits	2–70°
final no. of variables	97
unique data used	2574 $Fo^2 > 3\sigma\ (Fo^2)$
$R_{(F)} = \Sigma \lVert Fo \rvert - \lvert Fc \rVert / \Sigma \lvert Fo \rvert$	0.041
$Rw_{(F)} = (\Sigma w(\lvert Fo \rvert - \lvert Fc \rvert)^2 / \Sigma w Fo^2)^{1/2}$	0.059
Standard error in an observation of unit weight	3.1

Atomic co-ordinates with their estimated standard deviations are listed in Table II and selected interatomic intramolecular distances and bond angles in Table III. A perspective view of the structure is given in Figure 1.

RESULTS AND DISCUSSION

Reaction of the dithiosquarate ligand with palladium salts leads to the isolation of crystalline products of general formulation $M[Pd(dtsq)_2](H_2O)_n$ ($M = K_2$, Ba, or $(PPh_4)_2$). All complexes exhibit a bright

TABLE II

Table of positional parameters and their estimated standard deviations

Atom	x	y	z	B(A^2)
Pd	0.000	0.000	0.000	1.75(1)
K	0.5572(3)	0.1476(1)	−0.0153(3)	2.76(3)
S1	0.1260(3)	0.1336(1)	0.1026(3)	2.41(3)
S2	0.1177(3)	−0.0723(1)	0.2982(3)	2.30(3)
O1	0.4149(9)	0.1941(4)	0.568 (1)	3.3 (1)
O2	0.3997(9)	−0.0005(4)	0.754 (1)	2.8 (1)
O3	0.761 (1)	0.2204(5)	0.323 (1)	3.7 (2)
C1	0.2271(9)	0.991(5)	0.335 (1)	1.9 (1)
C2	0.222 (1)	0.0151(5)	0.416 (1)	2.0 (1)
C3	0.3342(9)	0.0370(5)	0.602 (1)	2.0 (1)
C4	0.339 (1)	0.1290(5)	0.514 (1)	2.2 (1)

Anisotropically refined atoms are given in the form of the isotopic equivalent thermal parameter defined as: $(4/3) \times [a^2 \times B(1.1) + b^2 \times B(2.2) + c^2 \times B(3.3) + ab(\cos\gamma) \times B(1.2) + ac(\cos\beta) \times B(1.3) + bc(\cos\alpha) \times B(2.3)]$

green color. However only the potassium salt displays a metallic luster.

Electronic spectra show maxima at 16 600, 28 900, 35 200, 37 590 (sh) and 46 300 cm^{-1}. They are characterized by a low-intensity *d-d* transition at 16 600 cm^{-1}, the other absorptions being related to charge-transfer or intraligand transitions. From a comparison with the spectrum of uncomplexed $(dtsq)^{2-}$, the band at 28 900 cm^{-1} may be attributed to a L → L* transition, while the whole spectrum is very similar to those of related dithiolene complexes.[9]

These complexes are found to display semi-conductive behavior with electrical conductivity measurements performed on pressed pel-

TABLE III

Selected interatomic distances (Å) and bond angles (deg) in $[Pd(C_4O_2S_2)_2]K_2$. 2H2O

Intramolecular distances and angles				
Pd	S_1	2.345(1)	S_1 Pd S_2	92.59(2)
Pd	S_2	2.320(1)	S_2 C_1 C_4	142.5 (2)
S_1	C_1	1.708(2)	S_2 C_2 C_3	141.2 (2)
S_2	C_2	1.715(2)	C_1 C_2 C_3	92.9 (2)
C_1	C_2	1.379(3)	C_2 C_3 C_4	87.3 (2)
C_2	C_3	1.463(3)	C_3 C_4 C_1	87.7 (2)
C_1	C_4	1.467(3)	C_4 C_1 C_1	92.2 (2)
C_3	C_4	1.508(3)		

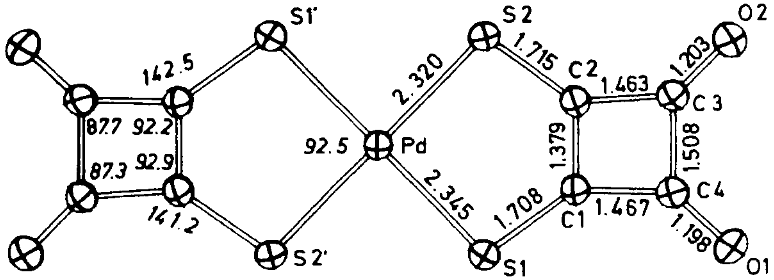

FIGURE 1 Structure of the $[Pd(C_4O_2S_2)]^{2-}$ dianion.

lets at room temperature of $\sigma = 2 \times 10^{-5}\,\Omega^{-1}cm^{-1}$ for the potassium salt and to 5.3×10^{-8} and $7 \times 10^{-8}\,\Omega^{-1}cm^{-1}$ for the barium and tetraphenyl phosphonium salts, respectively.

From static determinations of the magnetic susceptibility it may be concluded that the potassium complex is diamagnetic. However it is not e.p.r. silent. Samples from different batches show a broad low intensity featureless signal which is approximately centered at $g = 2.04$.

Description of the Structure.—The crystal structure consists of separate potassium cations, bis(dithiosquarato) palladate anions and water molecules. The structure of the anion shown in Figure 1, resembles the related Ni(II) complex previously described.[5]

The palladium atom lies on a crystallographic center of symmetry, it is coordinated in a square planar fashion to four sulfur atoms from two liigands. The whole complex anion is almost planar with a maximum distance of 0.05 Å to the mean plane which includes the metal center.

All bond distances are quite normal i.e. the average Pd-S value of 2.33 Å fits well with those found in the bis(ethylene-1-2-dithiolene)[10] and bis(dithiobenzoato) complexes[11] (2.314 and 2.32 Å, respectively). The average value of the C-S bonds (1.71 Å) is close to that observed in palladium thiourea complexes[12] and bis(ethylene-1-2-dithiolene)palladate[11] (1.70–1.71 Å) but slightly longer than the value found for the homologous nickel complex (1.69 Å).[5] All these values are consistent with a high degree of multiplicity of the C-S bonds. However it may be emphasized that, in the present case, the $C_1C_2C_3C_4$ quadrilateral is far from being regular. The C_2-C_1 bond is significantly shorter than the other carbon-carbon distances. This supports a description of the dithiosquarate anion that favours the mesomeric form *a* and, to a lesser extent, forms *b* and *c* (Figure 2). In spite of this shortening of the C_2-C_1 bond, the S_1-S_2 bite distance is larger in the palladium complex than in its nickel homologue.[5] Nevertheless both values are markedly shorter than the estimated constrained ligand bite of 3.75 Å and than the value of ca. 3.92 Å observed in a related polynuclear copper complex.[13]

Alkali cations and water molecules form separate stacks parallel to the crystallographic *c* axis.

The potassium cation exercises a marked influence on the separation of oxygen atoms O(1) and O(2) because these atoms belong to its coordination sphere. The potassium is surrounded by six oxygen atoms, two from water molecules and four from dithiosquarate groups (two $O(1)_i$ and $O(2)_i$ belonging to the same dithiosquarate), all of them at distances ranging from 2.74 Å to 2.92 Å.

The most interesting feature in this structure is the stacking of the planar anions along two parallel axes which are (i) the crystallographic *c* axis and (ii) an axis (d) issued from the center of the bc plane (Figure 3).

Within each stack, the anions eclipse each other and are inclined at $\omega = 56°$ to the stacking axis, so that the palladium environment, which appears square-planar within an anion, is actually a distorted octahedron with two centrosymmetrically related oxygen atoms from neighboring anions, one above and one below, at a Pd-O distance of 3.66 Å. More interestingly, the distance (3.51 Å) between two successive planes is greatly reduced with respect to the Pd-Pd spacing which is equal to the *c* parameter, i.e. 6.29 Å. An interplane separation of 3.51 Å is typical of systems with strong intermolecular π-orbital interactions. As a comparison, the stacking distance in the low-temperature metallic conductor [TTF] $[Ni(dmit)_2]_2$ is 3.55 Å. In addition, inspection of the structural data points to possible interstack interactions since the closest O. . .O and O. . .S distances (Figure 4) have values of 3.5–3.6 Å which are not far removed from the sum of Van der Waals radii. Given the two types of interaction, $[Pd(dtsq)_2]K_2$ cannot be viewed as a classical one-dimensional system but is best

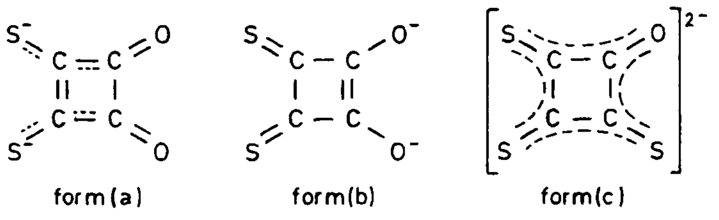

FIGURE 2 Possible forms for the dithiosquarate dianion.

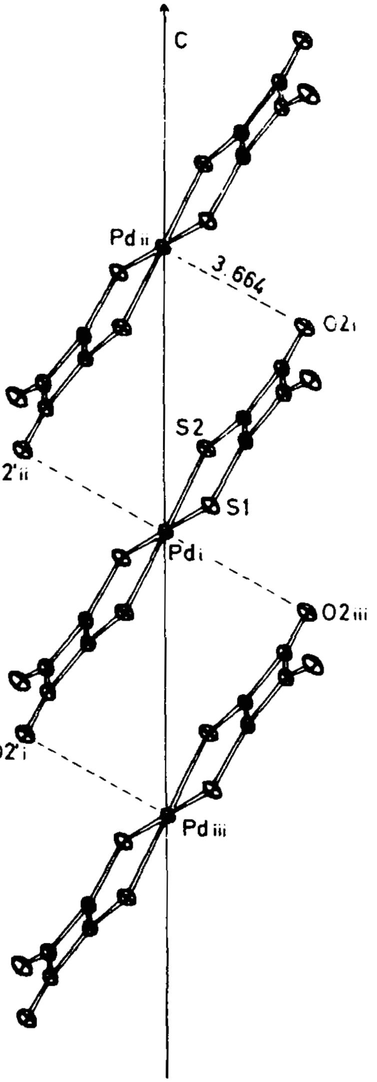

FIGURE 3 Stacking of the planar $[Pd(C_4O_2S_2)]^{2-}$ along the *c* direction.

described as a two dimensional material. Its structural arrangement is resembling that observed for the conducting complex $[NBu_4]_{0.29}[Ni(dmit)_2]$ recently described by Cassoux *et al.*[16] The same type of interstack contacts also exists in the low-pressure superconducting organic metals $(TMTSF)_2ClO_4$ and other salts of TMTSF

(TMTSF = tetramethyltetraselenafulvalene) as well as in tetrathiofulvalene derivatives.[17]

$K_2[Pd(dtsq)_2]$ meets the structural requirements for obtaining highly conducting systems, i.e. perfectly regular stacking and short intermolecular contacts, but not the most important electronic criterion, i.e. the pressence of a non-integral oxidation state, which is fulfilled in the case of Cassoux' compound. This clearly accounts for the low conductivity of $K_2[Pd(dtsq)_2]$ with respect to that of $[NBu_4]_{0.29}[Ni(dmit)_2]$.[16]

Although not usual for palladium complexes, the green color has so far been observed for two types of complexes, i.e. Magnus-type salts and dianionic 1,2-dithiolene complexes. It may be recalled that the green color of the Magnus-type salts has been considered to be

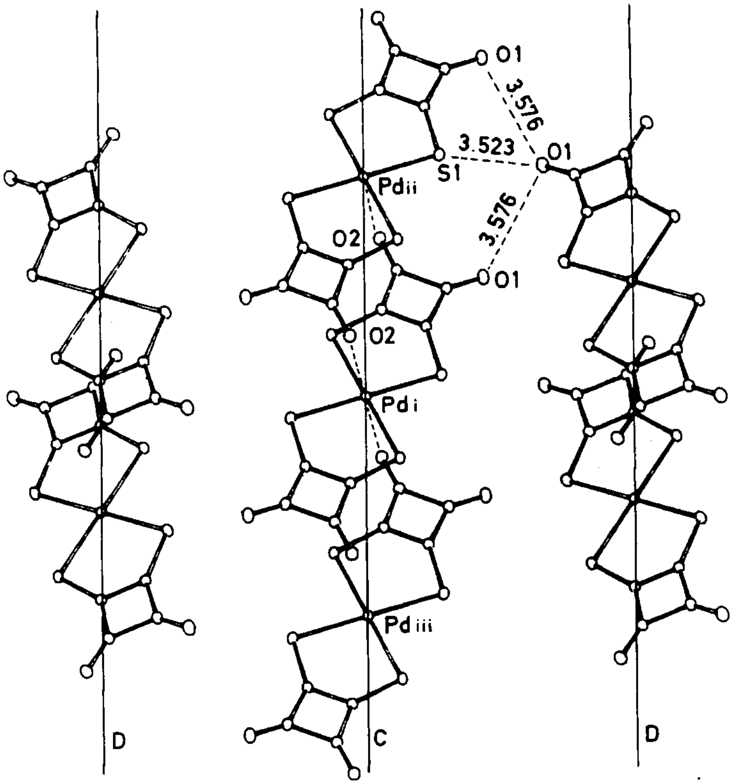

FIGURE 4 View along the *c* and *d* axis in order to show the various interstack contacts.

a diagnostic for strong metal-metal interactions.[18] Due to the large Pd. . .Pd distance (6.29 Å), such interactions are precluded in the case of $K_2[Pd(dtsq)_2]$. Since the color is retained in solution, it cannot originate in a solid-state structural peculiarity but must be related to the electronic structure of the molecular unit. This is supported by the close resemblance between the electronic spectrum of $[Pd(dtsq)_2]^{2-}$ and that of $Pd(S_2C_2(CN)_2]^{2-}$.[9] Both spectra show very intense charge-transfer and intraligand transitions. However, they do not overlap with the less-intense d-d transitions which therefore are easily located at 16 600 cm^{-1} and 15 700 cm^{-1} for the dithiosquarato and the dithiolato complexes, respectively. These d-d transitions are clearly responsible for the color of the two types of complexes.

Regarding the EPR signal, its low intensity together with the fact that static susceptibility measurements do not detect any paramagnetism suggest that it would arise from an "impurity." For Magnus green salt and tetracyanoplatinates, it has been suggested that the "unusual properties" would be extrinsic and caused by a small amount (ca. 200 ppm) of a platinum(IV) species.[19] The occurrence of traces of palladium(IV) in the present complexes is open to discussion but, in our opinion, may be ruled out for the following reasons:

(i) the higher oxidation state is less stable in the case of palladium than in the case of platinum;

(ii) the dithiosquarate ligand is known to be a reducing agent which would be hardly compatible with the presence of palladium(IV);

(iii) the EPR signal observed for Magnus green salt is anisotropic with g-values of ca. 1.94 and 2.50,[20] whereas for $K_2[Pd(dtsq)_2]$ the signal is practically isotropic (g ca. 2.04);

(iv) the intensity of the signal increases when amounts of $[PtCl_6]^{2-}$ are added to the originally "pure" Magnus green salt whereas similar doping experiment does not affect the signal of K_2 $[Pd(dtsq)_2]$.

As an alternate explanation, it could be conceivable that the impurity would originate in an oxidation of the ligand to give a radical. This would be consistent with the observation of an EPR signal centered around $g = 2.04$. Interestingly, oxidation of the dianionic complexes of 1,2-dithiolene yields monoanionic complexes which are paramagnetic and produce an almost isotropic EPR signal. From the relating g-value of ca. 2.04, it has been inferred that the orbital associated with the unpaired electron involves significant mixing of the ligand and metal *d*-orbitals.

Work is in progress to investigate the electrochemical properties of the $[Pd(dtsq)_2]^{2-}$ complexes and more specifically their eventual electron transfer reactions.

References

1. J. Miller and A. Epstein, *Prog. Inorg. Chem.*, **20**, 1 (1976).
2. (a) K. Krogmann, *Angew. Chem. Int. Ed. Engl.*, **8**, 35 (1969); (b) H. R. Zeller, *Adv. Solid State Phys.*, (Festközperprobleme), **13**, 31 (1973); (c) H. Nagasawa, *Phys. State Sol.*, **109**, 749 (1982).
3. A. R. Siedle, "Extended Linear Chain Compounds," vol. 2, 469 (1982), J. S. Miller Ed., Plenum Press, New York.
4. (a) P. S. Gomm, A. E. Underhill and D. M. Watkins, *J. Chem. Soc., Dalton Trans.*, 2309 (1972); (b) F. N. Lecrone and J. H. Perlstein, *J. Chem. Soc. Chem. Comm.*, 75 (1972); (c) A. H. Reis, Jr., S. W. Peterson and S. C. Lin, *J. Amer. Chem. Soc.*, **98**, 7839 (1976).
5. D. Coucouvanis, D. G. Holah and F. J. Hollander, *Inorg. Chem.*, **14**, 2657 (1975).
6. G. Maaks, *Justus Liebigs Ann. Chem.*, **686**, 55 (1965).
7. K. J. Euler, R. Kirchof and H. Metzendorf, *Materials Chemistry*, **4**, 611 (1979).
8. D. T. Cromer and J. T. Waber, "*International Tables for X-ray Crystallography*," J. A. Ibers and W. C. Hamilton Eds., Kynock Press: Birmingham, England (1974).
9. J. A. McCleverty, *Prog. Inorg. Chem.*, **10**, 49 (1968); S. Alvarez, R. Vicente and R. Hoffman, *J., Amer. Chem. Soc.*, **107**, 6253 (1985).
10. K. W. Browall, T. Bursh, L. V. Interrante and J. S. Kasper, *Inorg. Chem.*, **11**, 1800 (1972).
11. M. Bonamico and G. Dessy, *J. Chem. Soc., Chem. Com.*, 483 (1968).
12. D. A. Berta, W. A. Spofford, P. Boldrini and E. L. Amma, *Inorg. Chem.*, **9**, 136 (1970).
13. F. J. Hollander and D. Coucouvanis, *J. Amer. Chem. Soc.*, **99**, 6268 (1977).
14. TTF = tetrathiafulvalene 2-(1′,3′,-dithiol-2′-ylidene)-1,3-dithiole. H_2dmit = 4,5-dimercapto-1,3-dithiole-2-thione.
15. M. Bousseau, L. Valade, M.-F. Bruniquel and P. Cassoux, *Nouv. J. Chim.*, **8**, 3 (1984).
16. L. Valade, J. P. Legros, M. Bousseau, P. Cassoux, M. Garbauskas and L. V. Interrante, *J. Chem. Soc., Dalton Trans*, **783** (1985). P. Cassoux, L. Valade, M. Bousseau, J.-P. Legros, M. Garbauskas and L. V. Interrante, *Proc. Abano. Terme, Conf.*, June (1984).
17. K. Bechgaard, K. Carneiro, F. B. Rasmussen, M. Olsen, G. Rindorf, C. S. Jacobsen, H. J. Pedersen and J. C. Scott, *J. Amer. Chem. Soc.*, **103**, 2440 (1981), N. Thorup, G. Lindorf, H. Saling and K. Bechgaard, *Acta. Crystallogr. Sect. B*, **B 37**, 1236 (1981).
18. J. R. Miller, *J. Chem. Soc.*, 4452 (1961), ibid. 713 (1965); B. D. Silverman and B. A. Scott, *J. Chem. Phys.*, 63, 523 (1975).
19. G. M. Summa and B. A. Scott, *Inorg. Chem.*, **19**, 1079 (1980). F. Mehran and B. A. Scott, *Phys. Rev. Let.*, **31**, 99.
20. B. D. Silverman and B. A. Scott, *J. Chem. Phys.*, **63**, 518 (1975).

Supplementary material

Listings of anisotropic thermal parameters for $K_2Pd(C_4O_2S_2)_2$, $2H_2O$, observed and calculated structure factor amplitudes have been deposited.

Table of general temperature factor expression—U's

Name	U(1.1)	U(2.2)	U(3.3)	U(1.2)	U(1.3)	U(2.3)
Pd	0.0230(3)	0.0205(3)	0.0223(3)	−0.0003(3)	−0.0027(2)	−0.0006(3)
K	0.0466(9)	0.0259(7)	0.0314(8)	0.0005(8)	−0.0040(7)	0.0008(6)
S1	0.0365(9)	0.0226(8)	0.0307(8)	−0.0024(7)	−0.0101(7)	0.0039(7)
S2	0.0381(9)	0.0192(7)	0.0286(8)	−0.0019(7)	−0.0077(7)	0.0013(6)
O1	0.053(4)	0.028(3)	0.043(3)	−0.013(3)	−0.018(3)	0.001(3)
O2	0.043(3)	0.030(3)	0.032(3)	−0.002(3)	−0.011(2)	0.003(2)
O3	0.058(5)	0.038(3)	0.044(3)	0.017(4)	0.001(4)	0.025(3)
C1	0.023(3)	0.023(3)	0.026(3)	−0.000(2)	−0.004(3)	−0.000(2)
C2	0.025(3)	0.025(3)	0.024(3)	0.001(2)	−0.003(3)	−0.000(2)
C3	0.026(3)	0.025(3)	0.027(3)	0.001(3)	−0.003(3)	0.000(3)
C4	0.027(3)	0.024(3)	0.031(3)	−0.002(3)	−0.004(3)	0.002(3)

The form of the anisotropic thermal parameter is:
$\exp[-2\pi^2\{h^2a^2U(1,1) + k^2b^2U(2,2) + l^2c^2U(3,3) + 2hkabU(1,2) + 2hlacU(1,3) + 2klbcU(2,3)\}]$ where a, b and c are reciprocal lattice constants.

Table of root-mean-square amplitudes of thermal vibration in angstroms

Atom	Min.	Int'med.	Max.	Atom	Min.	Int'med.	Max.
Pd	0.136	0.144	0.165	O3	0.109	0.234	0.269
K	0.160	0.172	0.223	C1	0.137	0.151	0.176
S1	0.142	0.152	0.219	C2	0.140	0.158	0.172
S2	0.138	0.151	0.213	C3	0.147	0.158	0.177
O1	0.142	0.183	0.272	C4	0.152	0.154	0.191
O2	0.154	0.173	0.232				

Table of refined temperature factor expressions—Beta's

Name	B(1.1)	B(2.2)	B(3.3)	B(1.2)	B(1.3)	B(2.3)
Pd	0.00705(8)	0.00175(2)	0.0112(1)	−0.00010(9)	−0.0021(2)	−0.0002(1)
K	0.0143(3)	0.00221(6)	0.0157(4)	0.0002(2)	−0.0032(6)	0.0003(3)
S1	0.0112(3)	0.00192(6)	0.0154(4)	−0.008(2)	−0.0079(6)	0.0016(3)
S2	0.0117(3)	0.00164(6)	0.0143(4)	−0.0006(2)	−0.0061(6)	0.0005(3)
O1	0.016(1)	0.0024(2)	0.022(2)	−0.0042(9)	−0.014(2)	0.001(1)
O2	0.0132(9)	0.0026(2)	0.016(1)	−0.0008(8)	−0.009(2)	0.0013(9)
O3	0.018(1)	0.0032(3)	0.022(2)	0.005(1)	0.001(3)	0.010(1)
C1	0.0072(9)	0.0019(2)	0.013(1)	−0.001(8)	−0.003(2)	−0.000(1)
C2	0.0076(9)	0.0021(3)	0.012(1)	0.0003(8)	−0.003(2)	−0.000(1)
C3	0.0079(9)	0.0021(3)	0.013(1)	0.0004(8)	−0.002(2)	0.000(1)
C4	0.008(1)	0.0021(3)	0.015(2)	−0.0006(9)	−0.003(2)	0.001(1)

The form of the anisotropic thermal parameter is:
$\exp[-(B(1,1)h^2 + B(2,2)k^2 + B(3,3)l^2 + B(1,2)hk + B(1,3)hl + B(2,3)kl)]$.

Table of general temperature factor Expressions—B's

Name	B(1.1)	B(2.2)	B(3.3)	B(1.2)	B(1.3)	B(2.3)	Beav
Pd	1.82(2)	1.62(2)	1.76(2)	−0.02(2)	−0.21(2)	−0.05(2)	1.75(1)
K	3.68(7)	2.05(5)	2.48(6)	0.04(6)	−0.32(6)	0.06(5)	2.76(3)
S1	2.89(7)	1.78(6)	2.42(6)	−0.19(6)	−0.80(6)	0.31(5)	2.41(3)
S2	3.01(7)	1.52(5)	2.26(6)	−0.15(5)	−0.61(6)	0.10(5)	2.30(3)
O1	4.2(3)	2.2(2)	3.4(2)	−1.0(2)	−1.4(2)	0.1(2)	3.3(1)
O2	3.4(2)	2.4(2)	2.6(2)	−0.2(2)	−0.9(2)	0.2(2)	2.8(1)
O3	4.6(4)	3.0(3)	3.5(3)	1.3(3)	0.1(3)	2.0(2)	3.7(2)
C1	1.8(2)	1.8(2)	2.0(2)	−0.0(2)	−0.3(2)	−0.0(2)	1.9(1)
C2	2.0(2)	2.0(2)	1.9(2)	0.1(2)	−0.3(2)	−0.0(2)	2.0(1)
C3	2.0(2)	1.9(2)	2.1(2)	0.1(2)	−0.2(2)	0.0(2)	2.0(1)
C4	2.2(2)	1.9(2)	2.4(2)	−0.1(2)	−0.3(2)	0.2(2)	2.2(1)

The form of the anisotropic thermal parameter is:
$\exp[-0.25\{h^2a^2B(1,1) + k^2b^2B(2,2) + l^2c^2B(3,3) + 2hkabB(1,2) + 2hlacB(1,3) + 2klbcB(2,3)\}]$ where a, b and c are reciprocal lattice constants.