The crystal structure analysis shows the molecule to be (II) and that it adopts the expected chair-chair conformation. The bond lengths are all within the accepted ranges and the N–O length of 1.28 Å in the nitroxide group agrees with previous crystal structure analyses of these radicals [N–O (av.)=1.28 Å] (Rassat & Rey, 1973).

The geometry of the nitroxide group is of interest as this group has not been extensively studied. A summary of the results obtained so far (Rassat & Rey, 1973) suggests that in non-planar rings the nitroxide group is pyramidal, with the N–O bond at $19(2)^\circ$ to the C–N–C plane. The present structure shows an angle of $17.0 (5)^\circ$. The distortion from planarity is outwards from the body of the molecule as this does most to relieve steric interactions with the carbonyl group. By comparison, the carbonyl group is planar within experimental error.

The conformation of the molecule, although the expected twin-chair, shows some distortion from ideal geometry even when the effects of the sp^2 hybridized C(3) and N are considered. The bond angles at C(2), C(4), C(6), and C(8) are all opened by 3-4° and the torsional angles in the rings suggest considerable flattening of the rings, particularly round the nitroxide

group, where they are some 10° smaller than near the carbonyl group. This might be due to a greater flexibility in the C–N–C system of nitroxide radicals. Additional evidence for the distortion of the ring system is shown by the interplanar angle C(2)C(3)C(4)/C(6)NC(8) of 41.3 (7)^{\circ} which for an ideal 3,7-dione system would be less than 10° .

I thank Drs W. Motherwell and J. S. Roberts for supplying the crystals.

References

- International Tables for X-ray Crystallography (1968). Vol. III. Birmingham: Kynoch Press.
- Motherwell, W. B. & Roberts, J. S. (1972a). Chem. Commun. pp. 328-329.
- MOTHERWELL, W. B. & ROBERTS, J. S. (1972b). Tetrahedron Lett. pp. 4287–4289.
- POWELL, M. T. G. & GRIFFITHS, A. (1969). CRYSTAL 69 system of crystallographic programs, Portsmouth Polytechnic.
- RASSAT, A. & REY, P. (1973). Tetrahedron, 29, 1599-1603.
- ROBERTS, J. S. & THOMSON, C. (1972). J. Chem. Soc. Perkin II, 2129–2140.

Acta Cryst. (1974). B30, 1370

Tetraamminepalladium(II) Pyrazine-2,5-dicarboxylate

BY R. L. HARLOW AND S. H. SIMONSEN

Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712, U.S.A.

(Received 21 November 1973; accepted 2 January 1974)

Abstract. $[Pd(NH_3)_4]C_4N_2H_2(CO_2)_2$, $C_6H_{14}O_4N_6Pd$, M.W. 340.6, triclinic, $P\overline{1}$, a=7.145 (1), b=10.685 (1), c=3.771 (1) Å, $\alpha=99.10$ (1), $\beta=98.78$ (1), $\gamma=$ 97.90 (1)°, 23 °C, Z=1, $D_x=2.041$, $D_m=2.040$ g cm⁻³, V=277.07 Å³. Full-matrix least-squares refinement of 1268 observed reflections collected with $\theta-2\theta$ scans on a Syntex $P2_1$ yielded a final agreement index, R, of 0.038. Multiple hydrogen bonds are formed between the square-planar tetraamminepalladium(II) cations and the pyrazine-2,5-dicarboxylate anions.

Introduction. The unit-cell dimensions were determined by a least-squares refinement of 29 high-angle reflections (Cu $K\alpha_1 = 1.54050$, Cu $K\alpha_2 = 1.54433$ Å). The

Table 1. Atomic coordinates and thermal parameters with e.s.d.'s

Positional parameters are $\times 10^4$; β_{11} , β_{22} and β_{12} are $\times 10^4$; β_{33} , β_{13} and β_{23} are $\times 10^3$.

The thermal parameters are of the form $\exp\left[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23})\right]$.

	x	У	Z	β_{11}	β22	β_{33}	β_{12}	β_{13}	β_{23}
Pd	0	0	0	63 (1)	42 (1)	44 (1)	20 (1)	4 (0)	0 (0)
O(1)	4918 (6)	1699 (4)	5808 (12)	200 (11)	48 (4)	82 (4)	25 (5)	6 (2)	-2(1)
O(2)	7884 (6)	2781 (4)	6438 (13)	162 (11)	84 (5)	99 (5)	58 (6)	16 (2)	-1(1)
N(1)	2731 (7)	- 146 (5)	- 762 (14)	103 (10)	83 (6)	71 (5)	42 (6)	10 (2)	-1(1)
N(2)	842 (7)	1904 (5)	1974 (14)	134 (11)	64 (5)	63 (5)	22 (6)	6 (2)	2 (1)
N(3)	3676 (7)	3863 (4)	8759 (14)	102 (10)	51 (5)	85 (5)	13 (6)	8 (2)	-3(1)
$\mathbf{C}(1)$	6155 (9)	2682 (5)	6752 (15)	156 (14)	56 (6)	45 (5)	44 (7)	5 (2)	2 (1)
C(2)	5530 (8)	3913 (5)	8482 (15)	108 (12)	48 (5)	43 (4)	25 (6)	6 (2)	1 (1)
C(3)	6812 (8)	5039 (6)	9732 (18)	96 (12)	57 (6)	84 (6)	20 (7)	11 (2)	-1 (2)

	x	У	Z
H(1)	2695	-654	- 2926
H(2)	3323	- 489	1042
H(3)	3379	641	-740
H(4)	808	2337	113
H(5)	2033	2044	3274
H(6)	27	2180	3434
H(7)	7989 (96)	5116 (65)	9322 (190)

space group was assumed to be $P\overline{1}$ and this was confirmed by subsequent refinement. A colorless crystal of approximate dimensions $0.15 \times 0.12 \times 0.17$ mm was used in collecting data on a Syntex P21 automatic diffractometer with Mo $K\alpha$ radiation monochromated by a graphite crystal. The θ -2 θ scan technique was used with scan rates varying from 2.0 to 5.0° min⁻¹ depending in a direct manner on the intensity of the reflection. Background measurements were taken at both ends of the scan range, each for a time equal to onehalf of the scan time. Intensities of 1279 independent reflections were measured. Lorentz and polarization factors, a correction for variation in the standard reflections, and an absorption correction ($\mu = 16.56$, Mo $K\alpha$) were applied in converting the intensities into structure amplitudes. Standard deviations in the intensities, $\sigma(I)$, and hence in the structure amplitudes, $\sigma(F_o)$, were derived directly from counting statistics.

With only one molecule per unit cell, both the cation and anion must straddle a center of symmetry. The structure amplitudes were phased by placing the palladium atom at the origin of the unit cell; a Fourier map then revealed the positions of all other non-hydrogen atoms. The conventional R value for the isotropic fullmatrix least-squares refinement of these atoms was



Fig. 1. Bond distances and angles for tetraamminepalladium-(II) pyrazine-2,5-dicarboxylate.

0.088 (NUCLS: J. A. Ibers's modification of ORFLS). A difference map yielded somewhat distorted hydrogen-atom positions; with the exception of H(7), the hydrogen atom attached to the pyrazine ring, a refinement of these positions failed. The hydrogen atoms, H(1-6), of the ammine groups were then fixed at tetrahedral angles and at a distance of 0.90 Å from the nitrogen atoms, with orientations that agreed as closely as possible with those found on the difference map. All hydrogen atoms were assigned an isotropic thermal parameter of 5.0 Å². Conversion to anisotropic thermal parameters for the non-hydrogen atoms and subsequent refinement yielded a final conventional R value of 0.038.* The weights used in the refinement were $1/\sigma^2(F_{o})$; 12 reflections for which $I < 3\sigma(I)$ were assigned a weight of zero. The estimated standard deviation for an observation of unit weight was 4.4. A final difference Fourier map revealed no peaks larger than $0.2 \text{ e} \text{ Å}^{-3}$ except for a series termination peak of approximately 2.0 e $Å^{-3}$ between the palladium atoms along the c axis. The atomic scattering factors used for Pd, O, N and C atoms were those of Cromer & Waber (1965): the scattering factor for the Pd atom was corrected for $\Delta f'$ as given by Cromer (1965). For the hydrogen atoms, the scattering factors listed by Stewart, Davidson & Simpson (1965) were used. The final positional and thermal parameters are given in Table 1.

Discussion. The structure determination was undertaken because Brown & Dewar (1973), who supplied the crystal, speculated that the compound might be a polymer of the type $-(-Pd-pyrazine-)_n$. The structure analysis revealed that the compound was ionic with a square planar tetraamminepalladium(II) cation and a pyrazine-2,5-dicarboxylate anion as shown in Fig. 1; the hydrogen atoms, H(1-3) and H(4-6), attached to N(1) and N(2), respectively, have been omitted. No unusual bond distances and angles were found. The estimated standard deviations in the distances and angles of the non-hydrogen atoms are as follows: Pd-N, 0.005 Å; all other distances, 0.008 Å; N-Pd-N, 0.2° ; all other angles, 0.6° . The Pd–Pd distance (parallel to the c axis) of 3.771 Å is too long for significant metal-metal interaction.

The atoms of the pyrazine ring and C(1) form a nearly perfect plane from which the largest deviation is only 0.001 Å. A twist of approximately 2° has occurred about the C(1)-C(2) bond such that O(1) and O(2) of the carboxylate group deviate from the ring plane by -0.044 (4) and 0.046 (5) Å, respectively. With the Pd atom located at a crystallographic center of symmetry, the Pd and N atoms of the Pd(NH₃)²⁺ cation must be planar.

^{*} A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30348 (7pp.).Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH I 1NZ, England.



Fig. 2. Partial packing diagram.

Fig. 1 also shows (dashed lines) some of the interionic distances between possible hydrogen-donor atoms, N(1) and N(2), and hydrogen-acceptor atoms, O(1), O(2) and N(3); the dashed lines represent all distances less than $3 \cdot 3$ Å. In addition Fig. 2, a partial packing diagram, shows the relative orientation of the hydrogen atoms attached to N(1) and N(2) and gives a clearer indication of possible hydrogen bonds.

The authors would like to thank the Robert A. Welch Foundation for support of this work (Grant No. F-017); the diffractometer was purchased with funds provided by the National Science Foundation (Grant GP-37028).

References

BROWN, S. B. & DEWAR, M. J. S. (1973). Private communication.

CROMER, D. T. (1965). Acta Cryst. 18, 17-23.

- CROMER, D. T. & WABER, J. T. (1965). Acta Cryst. 18, 104-109.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). J. Chem. Phys. 42, 3175–3187.

Acta Cryst. (1974). B30, 1372

The Crystal Structure of Tetra-(2-thienyl)silane

BY ANASTAS KARIPIDES, A. THOMAS REED AND RAYMOND H. P. THOMAS Department of Chemistry, Miami University, Oxford, Ohio 45056, U.S.A.

(Received 27 December 1973; accepted 24 January 1974)

Abstract. (C₄H₃S)₄Si, tetragonal, $P\overline{4}2_1c$, $a=11\cdot368$ (9), $c=6\cdot535$ (5) Å, Z=2, $D_c=1\cdot42$, $D_o=1\cdot42$ (1) g cm⁻³ (by flotation in aqueous KI solution). The structure is orientationally disordered. Each thienyl ring has two conformations rotated 179° with respect to the Si–C(1) bond. The structure was refined by rigid-body leastsquares methods to $R=9\cdot1\%$.

Introduction. Colorless, elongated needle crystals of tetra-(2-thienyl)silane were grown by slow evaporation of a benzene solution from a sample kindly provided by Dr L. Spialter of the Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio. A single crystal of approximate dimensions $0.12 \times 0.12 \times 0.25$ mm was used. From indexed Weissenberg photographs the systematic absences h00 for h odd and hhl for l odd uniquely determined the space group to be $P\overline{4}2_1c$.

Three-dimensional intensity data were collected on a Picker FACS-1 diffractometer equipped with a scin-

tillation counter and pulse-height analyzer; zirconiumfiltered Mo $K\alpha$ ($\lambda = 0.71069$ Å) radiation was used. In total, 1159 reflections out to 55° in 2 θ were measured using the $\theta - 2\theta$ scan mode. In $P\overline{42}_1c$ the *hkl* and *khl* reflections are equivalent by symmetry for $h \neq k$. Averaging of the corresponding equivalent *hkl* and *khl* pairs yielded 540 reflections. There were an additional 79 *hhl* type reflections to give a total of 619 independent reflections. Of these, 497 had $I > \sigma(I)$ and were used in subsequent calculations.

The space group $P\overline{4}2_1c$ has eight general positions which requires that the two silicon atoms per unit cell be constrained at special positions of $\overline{4}$ symmetry. There is only one thienyl ring in the asymmetric unit. An electron-density map phased by the silicon atom revealed the essential features of the independent thienyl ring. However, attempts to improve the positions of the ring atoms with a series of difference Fourier syntheses proved unsuccessful. Each successive map gave consistently unrealistic bond distances