comporte comme un coordinat dont le cône d'encombrement serait ~5° moindre que celui de la tpP.

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Structure of β-Bis(1,2-benzoquinone dioximato)palladium(II), β-Pd(bqd)$_2$

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Abstract. Pd($C_6H_5N_2O_2$)$_2$, monoclinic, $P2_1/c$, a = 8·908 (6), b = 3·774 (2), c = 18·741 (10) Å, β = 92·51 (5)°, $Z = 2$, $V = 629$ Å^3, $d_c = 2·01$ Mg m^{-3}. The structure of the β modification has been solved from diffractometer data by Fourier methods and refined by a least-squares procedure to R = 0·052 for 636 observed reflections. The planar complex molecules stack along b, inclined at an angle of 25° relative to the b axis. The interplanar distance is 3·42 Å.

Introduction. α,β-Dione dioximato complexes of the Ni triad crystallize in highly anisotropic structures. They are closely related to the model compounds proposed by Davis, Gutfreund & Little (1976) for a possible high-temperature excitonic superconductor. These complexes crystallize in two possible modifications, either with their planes perpendicular, or inclined, relative to the stacking direction. Their properties have been reviewed by Thomas & Underhill (1972). Recent structural results have been summarized by Endres, Keller, Lehmann, Poveda, Rupp & van de Sand (1977). They showed that only rarely do such compounds crystallize in both modifications and they discussed the parameters which favor the one or other stacking pattern. One such example is Pd(bqd)$_2$. The α-form crystallizes in a perpendicular stacking mode (Leichert & Weiss, 1975*a*), similar to the structure of Pt(bqd)$_2$ (Mégnamisi-Bélombé, 1978*a*). On the other hand the crystal structure of the β-form, described in the following, resembles that of Ni(bqd)$_2$ (Leichert & Weiss 1975*b*), where the molecular planes are inclined relative to the stacking direction. The occurrence of these two modifications has been mentioned earlier (Endres, Keller, Mégnamisi-Bélombé & Nöthe, 1975; Endres, Keller, Lehmann, Poveda, Rupp & van de Sand, 1977). Differences in physical properties associated with the different stacking patterns have been studied by Mégnamisi-Bélombé (1978*b*) and Brill, Mégnamisi-Bélombé & Novotny (1978).

A procedure for the selective preparation of α- or β-Pd(bqd)$_2$ has not been established thus far. Both modifications form in varying ratios on cooling and/or

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evaporation from hot saturated solutions of Pd(bqd)$_2$. The α- or β-form can be recognized optically in large crystals. The crystals used in this study were grown as follows: 500 ml of a 3:1 mixture of *o*-dichlorobenzene (99%+, Eastman Kodak) and acetonitrile (Analyzed Reagent) heated at 393 K was over-saturated with about 700 mg of powdered Pd(bqd)$_2$. The dark-green hot solution was filtered quickly into a long-form glass beaker and maintained at ~403 K for some 2 h (under a watch-glass cover). The temperature was reduced to 353 K and then slowly to 303 K during the course of two weeks. The loosely covered beaker was allowed to stand undisturbed for another 10 d at this temperature. Crystals of β-Pd(bqd)$_2$ of length ~10 mm, recognizable by their black color and isotropic silvery reflectance, were selected from the crystals formed. These were washed with cold acetone and dried for several days at about 373 K.

A plate-like crystal with dimensions 0·2 × 0·13 × 0·03 mm was mounted on the top of a glass fiber. Orientation matrix and lattice constants were calculated from the setting angles of 15 reflections, centered on a computer-controlled four-circle single-crystal diffractometer (Syntex $P2_1$, Mo $K\alpha$ radiation, graphite monochromator). The lattice was checked for higher symmetry by a Delaunay reduction program. Intensity measurements ($P2_1$ diffractometer, θ–2θ scans, background-peak-background step scan mode, $2{\cdot}5 < 2\theta < 50°$, 1351 reflections) yielded 647 observed independent reflections with $I > 3{\cdot}0\sigma(I)$. Initially the data were corrected for Lorentz and polarization factors only, and statistical weights were assigned.

Calculations were carried out with programs of the Enraf–Nonius *Structure Determination Package* on a PDP 11/45 computer (Department of Chemistry, Stanford University). Scattering factors were derived from *International Tables for X-ray Crystallography* (1974), and anomalous terms were included. Plots were performed with the PDP 11/45–Versatec plotter adaption of Johnson's (1965) *ORTEP*.

The systematic extinctions ($h0l$ with l odd, $0k0$ with k odd) determine space group $P2_1/c$ uniquely, and with $Z = 2$ the asymmetric unit comprises one half of a complex molecule. Pd must occupy a special position, which is also shown by the fact that reflections hkl with $k + l$ odd are very weak. Thus Pd was placed at 0,0,0, and two subsequent Fourier syntheses revealed the positions of all the nonhydrogen atoms. Isotropic refinement converged at $R = 0{\cdot}076$; mixed refinement with anisotropic temperature factors for Pd only yielded $R = 0{\cdot}068$, anisotropic refinement 0·059. H positions were looked for unsuccessfully on a difference Fourier map, and were not included in the calculations.

Table 1. *Positional parameters*

	x	y	z
Pd(1)	0·0000 (0)	1·0000 (0)	0·0000 (0)
O(1)	−0·1177 (9)	0·813 (3)	0·1372 (4)
O(2)	0·3099 (8)	0·889 (2)	−0·0398 (4)
N(1)	0·2105 (9)	0·849 (3)	0·0118 (5)
N(2)	0·0032 (12)	0·818 (3)	0·0984 (5)
C(1)	0·132 (1)	0·690 (4)	0·1239 (6)
C(2)	0·158 (1)	0·542 (4)	0·1925 (6)
C(3)	0·301 (2)	0·420 (3)	0·2105 (7)
C(4)	0·422 (1)	0·434 (3)	0·1613 (7)
C(5)	0·400 (1)	0·590 (3)	0·0940 (7)
C(6)	0·245 (1)	0·717 (4)	0·0725 (6)

At this stage, data corrected for absorption became available [absorption coefficient 1·4747 mm^{-1}, crystal faces ±(100), ±(010), ±(001), grid size 14 × 20 × 2, transmission factors between 82·64 and 95·62%]. R then dropped to 0·057. Eleven reflections were rejected (with measured intensities just above the statistical threshold and with calculated ones much lower or with obvious measurement faults). Based on the remaining 636 intensities, R dropped after three final cycles to 0·052 (weighted $R = 0{\cdot}058$, maximum shift/error 0·03).

Atomic coordinates are listed in Table 1.* The numbering scheme of the centrosymmetric molecule as

Table 2. *Deviations with e.s.d.'s* (Å) *of atoms from a least-squares plane*

The equation of the plane is of the form $Ax + By + Cz - D = 0$ with $A = -0{\cdot}2317$, $B = -0{\cdot}9061$, $C = -0{\cdot}3540$, $D = -3{\cdot}4196$.

	Distance	E.s.d.
Pd	0·0	0·0
N(1)	0·006	0·010
N(2)	−0·017	0·012
O(1)	−0·001	0·012
O(2)	−0·003	0·009
C(1)	−0·011	0·014
C(2)	0·001	0·015
C(3)	0·007	0·013
C(4)	0·026	0·012
C(5)	−0·027	0·012
C(6)	−0·005	0·014

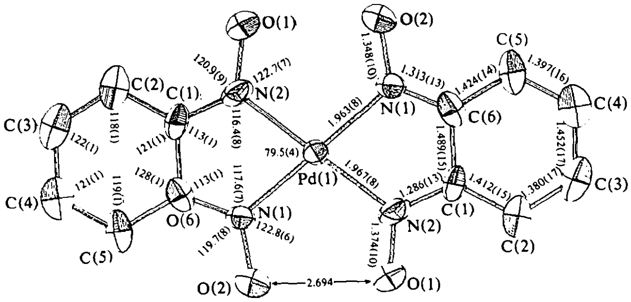

Fig. 1. *ORTEP* plot of bis(1,2-benzoquinone dioximato)-palladium(II) with bond lengths and angles. Thermal ellipsoids are at 40% probability (also in Figs. 2 and 3).

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33915 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

well as bond lengths and angles are shown in Fig. 1. Deviations of the atoms from a least-squares plane are given in Table 2. The complexes are stacked along *b*, the normal of the complex plane forms an angle of 25° with the *b* axis. The resulting perpendicular intermolecular distance is 3·42 Å. The 'herring-bone' kind of stacking of the complexes along $0,y,0$ and $0,\frac{1}{2}+y,\frac{1}{2}$ is depicted in Fig. 2, a *yz* projection of the structure. Fig. 3 shows two adjacent molecules within a stack, projected perpendicularly to their planes: the direction of the normal of the plane which determines the direction and the amount of 'slip' of a molecule with respect to its neighbor, apparently adjusts in a way to minimize the repulsion between the atoms of adjacent planes.

Discussion. The bond lengths correspond well to the values reported in the literature for bqd complexes. β-Pd(bqd)$_2$ closely resembles its Ni analogue by the slanted type of stacking, though the stacking direction is different [Ni(bqd)$_2$: $P2_1/n$, stacks along *a*: Leichert & Weiss, 1975*b*]. There are no strong intermolecular electronic interactions in this modification, in contrast to the α-modification (Leichert & Weiss 1975*a*), where a direct overlap of metal orbitals may occur. Thus, the α-form is 'one-dimensional' from an electronic point of view, whereas the β-form can only be termed anisotropic from a structural point of view. This is also illustrated by polarized reflectance spectra reported by Brill, Mégnamisi-Bélombé & Novotny (1977). These authors also reported a reversible phase transition in α-Pd(bqd)$_2$ at 90 K to a modification with a lower lattice symmetry (from elastic measurements and X-ray powder patterns). Since this low-temperature form is not identical with β-Pd(bqd)$_2$, there must be at least three modifications of this compound.

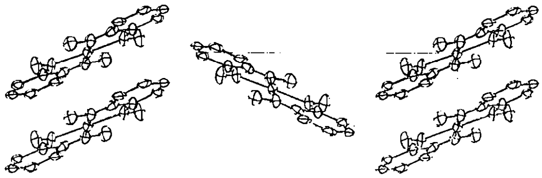

Fig. 2. Projection of the structure onto the *yz* plane, showing the 'herring-bone' stacking arrangement.

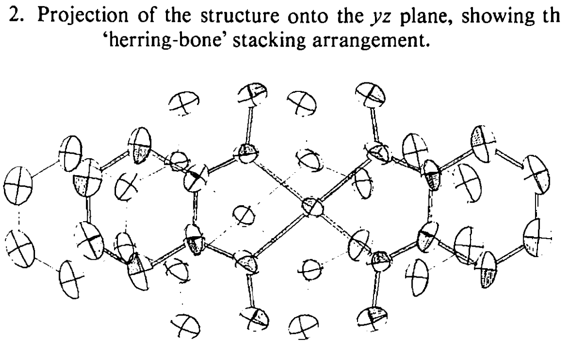

Fig. 3. Two adjacent molecules of one stack projected perpendicular to their planes.

There are only a few other examples of α,β-dione dioximato complexes of the Ni triad which crystallize in both the perpendicular and the inclined stacking mode: bis(ethylmethylglyoximato)nickel(II) (Sharpe & Wakefield, 1957; Bowers, Banks & Jacobson, 1972), bis(diethoxycarbonylglyoximato)platinum(II), and possibly bis(diphenylglyoximato)nickel(II) (Endres, Keller, Lehmann, Poveda, Rupp & van de Sand, 1977). These authors have stated that in the cases where both modifications occur in the same compound, the inclined one has the higher density. Hence this modification is favored by the packing forces. The perpendicular stacking mode is favored when bonding metal–metal interactions predominate. β-Pd(bqd)$_2$ agrees with this observation: its calculated density is 2·01 Mg m^{-3}, compared to 1·9 Mg m^{-3} for the α-form.

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