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The One-Dimensional Chain Structure of (1,2-Benzoquinone dioxime)diiodoplatinum(II), [PtI₂(C₆H₆N₂O₂)]

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Abstract. $M_r = 587.02$, triclinic, $P\bar{1}$, $a = 7.325$ (4), $b = 7.658$ (3), $c = 10.722$ (5) Å, $\alpha = 70.06$ (3), $\beta = 79.62$ (4), $\gamma = 76.12$ (4)°, $V = 545.7$ Å³, $Z = 2$, $D_x = 3.57$ g cm⁻³, $Mo K\alpha$, $\lambda = 0.71069$ Å, $\mu = 176$ cm⁻¹, room temperature, $F(000) = 512$, $R = 0.079$ for 2023 observed independent reflections. The planar complex molecules are stacked in a columnar fashion along a . Adjacent complexes within a stack are rotated by 180° along the stacking axis. An infinite Pt–Pt–Pt zigzag chain results, with Pt–Pt separations of 3.673 (2) and 3.707 (2) Å and a Pt–Pt–Pt angle of 166.0 (1)°.

Introduction. 1,2-Benzenedione dioxime (1,2-benzoquinone dioxime, H₂bqd) is known as an excellent ligand which readily forms bis-chelated transition-metal complexes, especially with the dipositive metal ions of the Ni triad (Mégnamisi-Bélobmé, 1978). In the special case of the Pt complexes, this ligand was observed to occur exclusively as the monoanion Hbqd⁻. Though

adducts of the form CuX₂·(H₂bqd) ($X = Cl^-, Br^-$) have been reported (Mégnamisi-Bélobmé, 1979), no analogues of Pt halides are known. This paper describes the synthesis and structure of PtI₂(H₂bqd). Its molecular structure closely resembles those of materials such as PtCl₂(bpy) (bpy = 2,2'-bipyridyl) which are suspected to be potential antitumour agents, based on the similarity of their structural characteristics to those of the anticancer drugs *cis*-dichloro(1,2-diaminoethane)-platinum(II) and *cis*-diamminedichloroplatinum(II) (Keller, 1982).

Experimental. Compound obtained as the product of a redox reaction whose mechanism is not clear. Excess molecular iodine (~2 g) dissolved in 400 ml acetone, 270 mg Pt(Hbqd)₂I₂ (Mégnamisi-Bélobmé, 1978; Pritzkow, 1976) added. Solution of 320 mg LiTCNQ† in 230 ml acetone filtered into this mixture. Mixture refluxed for 5 h, filtered hot, red-brown filtrate evaporated slowly over 10 d at room temperature.

* Correspondence about preparation and properties should be addressed to M. Mégnamisi-Bélobmé, about the structure to H. Endres.

† TCNQ = 7,7,8,8-tetracyano-*p*-quinodimethane = 2,2'-(2,5-cyclohexadiene-1,4-diyliidene)bis(propanedinitrile).

Crystals separated by filtration, washed with cold acetone. Flat, long, lustrous red-violet and slightly dichroic crystals moderately soluble in warm acetone. D_m not determined.

Crystal $0.025 \times 0.06 \times 0.25$ mm. Lattice parameters from setting angles of 35 reflections centred on a diffractometer (Siemens-Stoe AED 2, monochromated Mo $K\alpha$ radiation). θ - ω scans; $\frac{1}{6}$ of scan range on each side taken as background; $2\theta \leq 55^\circ$; $\pm h$, $\pm k$, $\pm l$; 2 check reflections at varying intervals, intensity variation $\pm 3.5\%$. Empirical absorption correction using ψ scans of 6 reflections, min. transmission factor = 0.19 (max. = unity). 4937 reflections measured and merged to 2481 independent; $R_{\text{int}} = 0.076$; 2023 with $I > 3\sigma(I)$ taken as observed; index range $h \pm 9$, $k \pm 9$, $l 0 \rightarrow 13$. Positions of Pt and I derived from Patterson map, other non-H atoms from Fourier synthesis. Refinement by full-matrix least squares based on F ; $w = 5.2/\sigma^2(F)$; anisotropic thermal parameters for Pt and I; max. $\Delta/\sigma = 0.02$, $R = 0.079$, $wR = 0.070$, $S = 10.8$; largest features in final difference Fourier map $+5.6$ and -3.6 e \AA^{-3} . Attempts to refine light atoms with anisotropic thermal parameters resulted in unreasonable thermal ellipsoids and gave no significant reduction of R . H positions not determined. *STRUCSY* (Stoe, 1984) program system on an Eclipse computer. Scattering factors including anomalous dispersion from *International Tables for X-ray Crystallography* (1974). Plots on a Tektronix plotter using *SHELXTL* (Sheldrick, 1983) on a Nova 3 computer.

Discussion. Atomic coordinates are listed in Table 1.* Fig. 1 shows the $\text{PtI}_2(\text{H}_2\text{bqd})$ molecule with bond distances and angles. The molecule is planar, max. deviation from least-squares plane 0.10 (5) \AA .

The complex molecules are stacked on top of each other along **a**. Adjacent molecules within a stack are related by an inversion centre so that the H_2bqd ligands point in opposite directions. A stereoview is shown in Fig. 2. The Pt atoms form a slightly zigzagged chain, with Pt-Pt separations of 3.673 (2) and 3.707 (2) \AA and a Pt-Pt-Pt angle of 166.0 (1) $^\circ$. Along a stack, the molecules are equally spaced, with intermolecular distances of 3.69 (6) and 3.63 (6) \AA . Fig. 3 (deposited) shows a view of two adjacent molecules of a stack perpendicular to their mean planes. The second overlap pattern looks very similar.

This structure closely resembles that found in many other $\text{PtX}_2(\text{LL})$ compounds, where *LL* represents two monodentate or one bidentate amino ligand (Keller, 1982). Some of these compounds are reported to occur

* Lists of structure factors and anisotropic thermal parameters and Fig. 3 have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39940 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

in different modifications. One form has the columnar structure as found in the title compound; the structure of the other form is different. We note that the batch of crystals used for this investigation contains some bright-red crystals which apparently are a different

Table 1. *Atom coordinates* ($\times 10^3$) *and isotropic temperature factors* ($\text{\AA}^2 \times 10^3$) (equivalent isotropic values for Pt and I)

U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}/U
Pt	248.7 (1)	986.5 (1)	22.2 (1)	22 (1)
I(1)	299.5 (3)	628.3 (2)	150.1 (2)	36 (1)
I(2)	181.8 (3)	1069.1 (3)	243.2 (2)	39 (1)
N(1)	293 (3)	959 (3)	-164 (2)	29 (5)
N(2)	208 (3)	1278 (3)	-108 (3)	42 (5)
O(1)	336 (3)	803 (3)	-194 (2)	48 (5)
O(2)	167 (3)	1413 (3)	-62 (2)	41 (5)
C(1)	278 (4)	1101 (4)	-257 (3)	32 (5)
C(2)	239 (4)	1282 (4)	-222 (3)	35 (5)
C(3)	200 (6)	1454 (6)	-321 (4)	78 (5)
C(4)	248 (5)	1464 (5)	-457 (4)	68 (5)
C(5)	290 (4)	1289 (4)	-495 (3)	48 (5)
C(6)	298 (4)	1117 (5)	-399 (3)	55 (5)

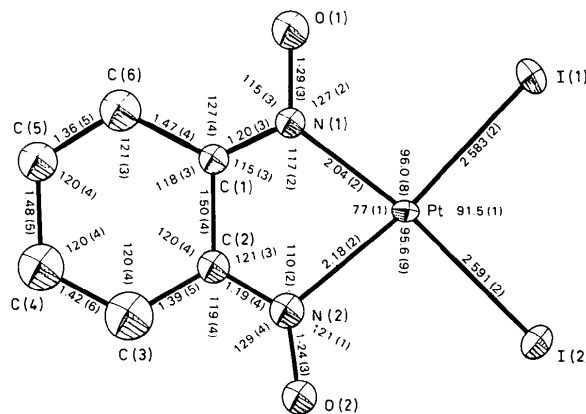


Fig. 1. The $\text{PtI}_2(\text{H}_2\text{bqd})$ complex molecule with bond distances (\AA) and angles ($^\circ$). Thermal contours are at 30% probability.

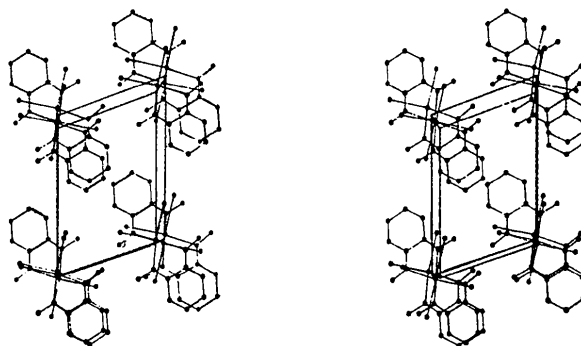


Fig. 2. Stereoscopic view of the structure from a direction inclined at 5° to **a**.

modification. From rotation photographs it appears that this modification also has a stacked structure, with a repeat distance of 7.40 (5) Å along the stacks. This can be deduced from the typical sequence of strong even, and weak odd layer lines. Poor crystal quality prevents further investigations.

The Pt^{IV} in the starting material has been reduced to Pt^{II} despite the presence of molecular iodine in excess. By analogy with other MX_2 (dioxime) complexes ($M = Ni, Pd, Pt$) it is assumed that H₂bqd is present as a neutral molecule in the title compound. The assignment of the oxidation state of +2 to Pt is also favoured by the square-planar coordination. The species oxidized in this redox process is most likely to be TCNQ⁻.

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The Structure of Trialuminium Tris(orthophosphate) Hydrate, AlPO₄-21, with Clathrated Ethylenediamine, Al₃(PO₄)₃·C₂H₈N₂·H₂O, and Pyrrolidine, Al₃(PO₄)₃·C₄H₉N·H₂O

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Abstract. AlPO₄-21(en): $M_r = 444.0$, monoclinic, $P2_1/n$, $a = 8.472$ (3), $b = 17.751$ (6), $c = 9.062$ (3) Å, $\beta = 106.73$ (3)°, $U = 1305$ (1) Å³, $Z = 4$, $D_x = 2.26$ g cm⁻³, Mo $K\alpha$, $\lambda = 0.7107$ Å, $\mu = 7.21$ cm⁻¹, $F(000) = 914$, room temperature, non-hydrogen atoms refined anisotropically to $R = 0.045$ for 2612 reflections with $I > 3\sigma(I)$. AlPO₄-21(py): $M_r = 455.0$, monoclinic, $P2_1/n$, $a = 8.668$ (1), $b = 17.558$ (2), $c = 9.186$ (2) Å, $\beta = 107.75$ (1)°, $U = 1333.7$ (5) Å³, $Z = 4$, $D_x = 2.27$ g cm⁻³, Mo $K\alpha$, $\lambda = 0.7107$ Å, $\mu = 7.07$ cm⁻¹, $F(000) = 920$, room temperature, non-hydrogen atoms refined anisotropically and H positions calculated; $R = 0.071$ for 2112 reflections with $I > 0.0$. Al^{IV} and P^{IV} form ribbons of edge-shared three- and five-membered rings along [101], which are joined along [010] *via* four-membered rings to form corrugated sheets of [Al₂P₂^{IV}O₇·H₂O] or [Al₂P₂^{IV}O₇·OH].

These sheets are cross linked by crankshaft-shaped single chains of strictly alternating Al- and P-centred tetrahedra at $y \simeq \frac{1}{4}, \frac{3}{4}$ to form an open network of channels in (010) bounded by eight-membered-ring apertures. The framework topology suggests a model for AlPO₄-25, the molecular sieve produced upon calcination of AlPO₄-21.

Introduction. A new series of aluminophosphate framework structures (designated AlPO₄- n , where n denotes a specific structure type) has been synthesized (Wilson, Lok & Flanigen, 1982; Wilson, Lok, Messina, Cannan & Flanigen, 1982) using various amines as 'templating agents'. A structure-directing role is presumed for the agent added to the starting aluminophosphate gel, which is treated hydrothermally at between 423 and 523 K. Many of the compounds are