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Evidence for Intrinsic Electrical Conduction in the Linear Metal-Chain Semiconductor Bis(1,2-benzoquinonedioximato)platinum(II), Pt(bqd)$_2$*

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The four-electrode dc conductivity of single crystals of the linear metal-chain compound bis(1,2-benzoquinonedioximato)platinum(II), Pt(bqd)$_2$, measured parallel to the long axis of the crystals, reveals ohmic behavior over the temperature range 77–550°K, and averages to $\bar{\sigma} = 3.3 \times 10^{-3}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ at room temperature. Unlike the well-characterized Magnus' Green Salt (MGS), $Pt(NH_3)_4PtCl_4$ ($\bar{\sigma} = 5.5 \times 10^{-4}\ \Omega^{-1}\ \mathrm{cm}^{-1}$), the present compound is found to be an intrinsic, small band gap semiconductor. The Pt–Pt distance of 3.180 Å, the shortest yet observed in Pt(II) glyoximates, was determined by powder X-ray diffraction. The small band gap is related to the unusually high conductivity of Pt(bqd)$_2$, which is most reasonably interpreted in terms of this short Pt–Pt separation. Preliminary results of polarized single crystal reflectance spectra demonstrating the anisotropic behavior of this compound are presented.

Because of their peculiar one-dimensional behavior (especially with respect to their electrical conduction), linear chain solids are now being widely studied, both by chemists and physicists, as a major focus in solid state research (*1–4*). In the category of stacked square planar complexes, the so-called Krogmann metals represent the most popular examples of such one-dimensional conductors (*5*). The pure d^8 complexes which yield the Krogmann metals upon partial oxidation crystallize also in a columnar structure; their electrical conductivity, however, is at most as large as that of very poor semiconductors (*6*). The most familiar example of a stacked d^8 system that exhibits a relatively high conductivity parallel to the stacking direction is the Pt(II) compound known as Magnus' Green Salt (MGS) (*7*). There has been, however, some disagreement concerning the correct interpretation of the conduction mechanism in this interesting compound. Whereas Miller understood this conduction to be an "intrinsic" process (*8*), more recent investigations (*9*) interpreted it in terms of "extrinsic" Pt(IV) impurity ions (guessed on the order of ppm) present in the host lattice. The main concern of the present study is to provide a new example of such a stacked Pt(II) system exhibiting intrinsic, unusually large semiconducting properties along the stacking direction.

In the past few years, our search for new Krogmann type compounds has been based on divalent d^8 metal complexes. For this purpose, we have selected the electrophilic aromatic molecule, 1,2-benzoquinonedioxime (bqdH), as a versatile chelating ligand system that is, in addition, particularly appropriate for a promising new approach to the synthesis of Little's excitonic high temperature superconductor (*10–11*). Thus, in the first stage of our synthetic work, we were successful in isolating

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a number of new stacked d^8 complexes of the general formula $M(\text{bqd})_2$ ($M = \text{Ni}^{2+}$, Pd^{2+}, Pt^{2+}; bqd^- = ion of bqdH) (*12*), and to partially oxidize the Ni and Pd derivatives such as to include linear polyiodine chains in the host lattice (*12a, 13*).

In this note we wish to present the results of the electrical conductivity of Pt(bqd)_2. This linear metal-chain compound crystallizes in long, rectangular black prisms (*12a, 13a*) exhibiting a marked anisotropic silvery luster that is polarized perpendicular to the long axis of the crystals. The dc conductivity, σ, measured along this axis is unusually high for a pure d^8 complex in a neutral molecular environment. The observed room temperature average value of $\bar{\sigma} = 3.3 \times 10^{-3}\ \Omega^{-1}\ \text{cm}^{-1}$ is several decades larger than in analogous platinum glyoximates (*15*), and is slightly higher than the average value of $\bar{\sigma} = 5.5 \times 10^{-4}\ \Omega^{-1}\ \text{cm}^{-1}$ previously reported for the extensively studied MGS (*9a*). Moreover, we show in the subsequent discussion that the conductivity of Pt(bqd)_2 is not affected by Pt(III) impurities, in contrast to recent observations in MGS (*9*).

Previous X-ray investigations (*16*) have shown Pt(bqd)_2 to be isomorphous with its palladium analog, α-Pd(bqd)_2, crystallizing in the orthorhombic system (space group *Imcb*) (*12b*). In the present study, the structures of both Pt(bqd)_2 and α-Pd(bqd)_2 were reexamined by powder X-ray diffraction methods. The results summarized in Table I indicate that the two compounds are isostructural rather than isomorphous, i.e., their overall symmetry is the same, but their respective cell dimensions differ substantially from one another. A complete three-dimensional X-ray structure analysis for Pt(bqd)_2 is currently in progress. From the three-dimensional precession graphs, the orthorhombic symmetry and the space group *Imcb* have been confirmed, and the cell constants for this compound are in excellent agreement with the results of the powder diffraction analyses. These analyses were performed using a Norelco Diffractometer with a graphite monochromator set for Cu$K\alpha$ radiation, and the stacking direction of the square planar complexes coincides with the crystallographic *a* axis. For α-Pd(bqd)_2 in Table I, note the excellent agreement of the present data with those of reference (*12b*) given in parentheses. Note, furthermore, that the Pt–Pt separation of only 3.180 Å is the shortest reported yet for Pt(II) compounds of this type. This may be related to the strong electron accepting ability of the electrophilic ligand moieties that delocalize the *d*-shell electrons of the Pt to a larger extent than those of the more rigid Pd shell. A possible mechanism for this delocalization may be provided by the backbonding formalism (*17*), whereafter filled *d* orbitals (mainly d_{xz} and d_{yz}) of the central metal hybridize with empty π^* orbitals of the coordinating ligand atoms, allowing for the *d* electrons of the metal to penetrate into

TABLE I

UNIT CELLS PARAMETERS FOR ORTHORHOMBIC Pt(bqd)_2 AND α-Pd(bqd)_2[a]

	$\text{Pt(bqd)}_2 : \text{Pt}(\text{C}_6\text{H}_5\text{O}_2\text{N}_2)_2$ mol. weight 469.33	α-$\text{Pd(bqd)}_2 : \text{Pd}(\text{C}_6\text{H}_5\text{O}_2\text{N}_2)_2$ mol. weight 380.64
a (Å)	6.361 ± 0.005	6.405 ± 0.001 (6.405)
b (Å)	9.663 ± 0.02	9.728 ± 0.004 (9,728)
c (Å)	20.837 ± 0.14	20.679 ± 0.03 (20.649)
Volume (Å^3)	1280.70	1288.42 (1286)
M–M distance = *a*/2 (Å)	3.180 ± 0.003	3.202 ± 0.001 (3.202)

[a] Values in parentheses are the three-dimensional single crystal data from Ref. (12*b*).

the sphere of the electron poor ligands. Thus, as a result of the d–π^* hybridization, the d-shell electron density of the central metal is reduced to some extent. Consequently, van der Waals repulsions between neighboring Pt atoms within a chain are appreciably lessened so that these atoms may move much closer to each other. In other words, this expansion of the d-electron "cloud" from the central metal to the ligand moieties (nephelauxetic effect) causes the Pt–Pt separation to decrease substantially and the interband gap E_g between valence and conduction band to decline significantly. Thus, the unusually large conductivity of $Pt(bqd)_2$ is best understood on the basis of this nephelauxetic effect. For more concrete interpretation of the conduction process, however, detailed band structure calculations lacking at present are needed.

For the main purpose of this work which was to establish the "intrinsic" behavior of $Pt(bqd)_2$, i.e., whether or not Pt(IV) "impurity" ions are responsible for its large electrical conductivity, different batches of this compound were prepared starting from Pt(II) as well as from Pt(IV) salts in water/acetone or *o*-dichlorobenzene solutions. As displayed in Table II, all the preparations yielded the same Pt(II) product, namely, $Pt(bqd)_2$, which was unambiguously identified by excellent microanalysis, ir spectra and chemical reaction with bromine (Br_2) or iodine (I_2) (*12a*). Purification of the crude products was effected by careful recrystallization from *o*-dichlorobenzene ("highest purity," 99%+, Eastman Kodak) or nitrobenzene, and crystal growth by the slow cooling of saturated hot solutions in the same solvents. Single crystals with typical dimensions 5 × 0.2 × 0.1 mm were used for the conductivity measurements. The conventional four-electrode conductance method was employed to measure the dc conductivity parallel to the long axis of several crystals from the various preparations over the temperature range 77–550°K. Gold wires of about 25 μm diameter served as the leads, and colloidal graphite (aquadag) or silver paste (electronic grade, Du Pont de Nemours) as the contacts. The temperature was regulated using a copper–constantan thermocouple connected to an electronic heater.

The specific conductivity, σ, measured this way for 25 different crystals ranged from 1.1×10^{-4} to $4.3 \times 10^{-2}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ at room temperature. The conductivity was not affected by the contact material, i.e., the values of σ obtained using aquadag were, within experimental error, identical to those observed using silver paste.

TABLE II

VARIOUS WAYS OF SYNTHESIZING $Pt(bqd)_2$

Batch No.	Platinum salt		Ligand		Complex
(I)	$K_2Pt^{II}Cl_4$	+	bqdH	→	$Pt^{II}(bqd)_2$
(II)	$K_2Pt^{IV}Br_6$[a]				
(III)	$K_2Pt^{II}Br_4\ 2H_2O$				
(IV):	prepared from $Pt^{II}(bqd)_2$ + $Pt^{IV}(bqd)_2Br_2$ in *o*-dichlorobenzene[b,c]				

[a] The reaction of bqdH and $K_2Pt^{IV}Br_6$ in warm water/acetone solution is a redox process that yields essentially $Pt^{III}(bqd)_2$ and probably Br_2 (*18*).

[b] In the Pt(IV) species, $Pt(bqd)_2X_2$(X = I^-, Br^-), the platinum is octahedrally coordinated to the coplanar bqd^- moieties and to the axially linked halogenides (*19*).

[c] A 3:2 molar mixture of $Pt(bqd)_2$ and $Pt(bqd)_2Br_2$ in hot *o*-dichlorobenzene solution resulted in separate recrystallization of the components on cooling the solution, a situation which is quite similar to the recent observations made with the analogous platinum diphenylglyoximates (*20*).

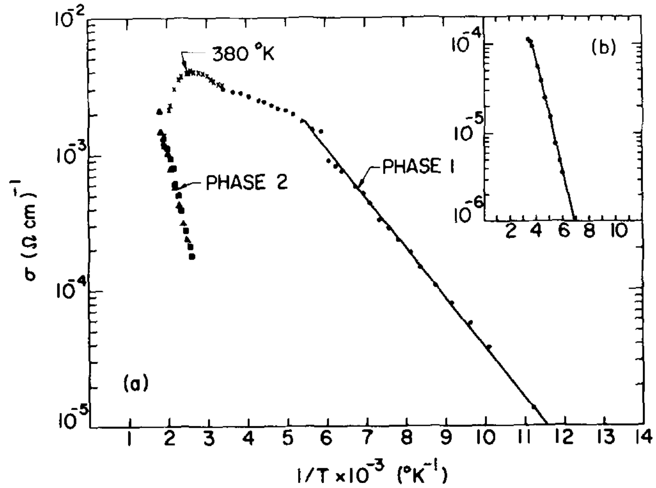

FIG. 1. Temperature dependence of the conductivity of $Pt(bqd)_2$, $\log\sigma$ vs $1/T$. (a) Batch (I): dots = cooling and heating curve between room temperature and liquid N_2; crosses = heating from room temperature to 240°C; squares = cooling from 240 to 110°C; triangles = heating from 110 to 275°C; at 278°C the crystal decomposed. (b) Batch (II): cooling and heating curve between room temperature and liquid N_2.

The temperature dependence of σ for two representative crystals selected from batch (I) and batch (II), respectively, is shown in Fig. 1. Plots of $\log\sigma$ vs $1/T$ yielded straight lines over a wide temperature range, consistent with ohmic semiconducting behavior. As typified by curve (a), a dramatic change obviously occurs above 380°K leading to a sharp decrease of the conductivity with increasing temperature. This behavior is reminiscent of an irreversible phase transition, very much like the transition recently observed in *N*-methylquinolinium(tetracyano-*p*-quinodiamethane)$_2$, $NMeQn(TCNQ)_2$ (*21*). Efforts to establish the true nature of the phase transition in $Pt(bqd)_2$, however, are currently in progress.

Assuming intrinsic conduction mechanism in the view of the Bloch-band theory model, a band gap $E_g = 0.25$ eV was calculated from the slope of curve (b), the corresponding E_g values for phase 1 and phase 2 of curve (a) being 0.15 and 0.55 eV, respectively. Thus, the unusually high conductivity of $Pt(bqd)_2$ is most reasonably interpreted on the basis of this small band gap which, in turn, arises as a result of the short Pt–Pt separation. If "extrinsic" acceptor impurities were to dominate the conductivity of $Pt(bqd)_2$, then one would expect crystals of batch (II) and batch (IV), which were deliberately prepared starting from Pt(IV) salts, to be more "impure" and hence to exhibit the highest conductivities (since in this case the acceptor impurity concentrations should be many orders of magnitude higher than parts-per-million amounts). On the contrary, these crystals turn out to be even less conductive than those of batches that were prepared starting from "pure" Pt(II) ions. This observation, therefore, clearly indicates that the presence of Pt(IV) ions during sample preparation does *not* affect the conduction mechanism in $Pt(bqd)_2$. Thus, conductivity fluctuations observed from batch to batch or within the same batch of this compound are to be interpreted merely as the result of crystalline imperfections or experimental errors. Another strong support for the "intrinsicality" of this new one-dimensional semiconductor was provided by the absence of an epr signal in all of the samples examined in this work, when the corresponding crystals were grown under sufficiently "clean" conditions to prevent contamination with paramagnetic impurities. In other words, the doping of Pt(IV) acceptor impurities into the Pt(II) atom chains observed in MGS (*9*) and giving rise to the

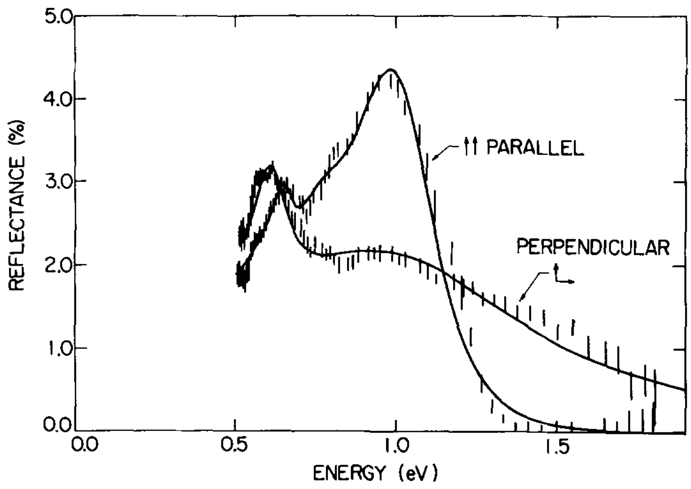

Fig. 2. Polarized single crystal reflectance spectra of Pt(bqd)$_2$: experimental data (broken lines) and fittings (solid lines) to these data.

formation of "localized" paramagnetic Pt(III) states, is apparently not likely to occur in Pt(bqd)$_2$.

Worthy of mentioning are, finally, the polarized single crystal reflectance spectra displayed in Fig. 2. In the parallel polarization, a broad absorption band is observed with a well-defined sharp edge at ~1.15 eV on the high energy side of the spectrum. We tentatively identify this absorption as the electronic interband transition from the $5d_{z^2}$ valence band to the $6p_z$ conduction band in a direct optical process. Thus, this band gap is about four times less than the analogous gap recently calculated for MGS (*22*). The fact that the electronic absorption band seen in the parallel polarization is no longer present in the perpendicular spectrum clearly demonstrates the anisotropic nature of Pt(bqd)$_2$. The smaller band gap energy obtained from the conductivity measurements may be associated with an indirect (phonon-assisted), thermal activation process. More concrete correlations of these quantities, however, must await detailed energy band calculations in order to be made.

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