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An Effective Core Potential ab Initio Study of Electronic Structure and Bandwidth−Charge Transport Relationships in Low-Dimensional, Partially Oxidized Palladium Glyoximates

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Ab initio calculations on cofacial dimers of palladium bis(glyoximates) are reported and are used to rationalize the temperature-dependent conductivity of the low-dimensional, partially-oxidized material $Pd(dpg)_2^{0.20+}(I_5^-)_{0.20}$ (dpg = diphenylglyoximato). The band structure near the Fermi level is dominated by two bands, of b_{3g} and a_u symmetry in the dimer, that arise from the ligand π orbitals. Near the observed $(dpg)_2Pd-Pd(dpg)_2$ staggering angle (90°), the b_{3g} bandwidth is zero, and the a_u band exhibits sharp variations with librational (twist) motion about the intermolecular Pd−Pd vector. This in turn, combined with the narrow bandwidth (calculated to be ~0.60 eV in a tight-binding model) implies that the electronic states are localized and that the material should be a hopping semiconductor rather than a molecular metal, in agreement with experiment.

Introduction

Recent years have witnessed great progress in the synthesis, characterization, and understanding of low-dimensional molecular substances with high electrical conductivity.[2] Among these classes of materials, partially oxidized, stacked metallomacrocyclic systems[3] such as square-planar bis(glyoximates),[4] bis(benzoquinone dioximates),[5] dibenzotetraazaannulenes,[6] phthalocyanines,[3,7,8] and porphyrins[9] represent a particularly rich, informative, and diverse subset. The solid state structural, optical, magnetic, and electrical properties of these materials have been studied in considerable depth. It is precisely because of this substantial data base that high-quality quantum chemical descriptions of the electronic structures are of great value in understanding the metallomacrocyclic architectural and stacking dependence of the physical properties.

Within the framework of a simple "tight-binding" band structure model,[10] the electrodynamical properties of low-dimensional conducting materials can be related to favorable overlap between frontier orbitals of the stacked units modulated by the particular spatial orientation and chain structure existing in the crystal. Segregated stacking of the molecular electron donor and acceptor subunits may favor intermolecular interactions involving either metal-based or ligand-based orbitals so that charge transport may be due to interactions involving metal d and/or ligand π orbitals.[2] Two extreme cases are represented by the stacked, mixed-valent tetracyanoplatinate salts and by the partially oxidized phthalocyanines. In the former, charge transport occurs through chains of metal atoms[11] (intermolecular

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interactions of metal d_{z^2} orbitals), while, in the latter, the major transport pathway is, in most cases, through overlapping macrocycle π systems.[7,8,12,13] This is most clearly evident in the properties of the metal-free phthalocyanine conductor $H_2(Pc)(I_3)_{0.33}$.[7e,g,8a] These low-dimensional systems exhibit, however, relatively narrow bandwidths[2,7,14] so that coupling of the conduction electrons to intramolecular vibrations as well as to intermolecular phonons and/or librations can effectively contribute to the resistivity along the chain.[15]

In spite of the large variety of theoretical studies devoted to understanding the properties of metallomacrocyclic conductors,[12-18] ab initio electronic structure calculations on stacked 4d complexes have not been reported. Such a theoretical approach, within the framework of a cluster model approximation,[14,15,19] allows an accurate analysis of HOMO–HOMO interactions in simple cofacial dimers that, in turn, can be straightforwardly extrapolated to the tight-binding bandwidth in the corresponding 1-D chain.[14,15]

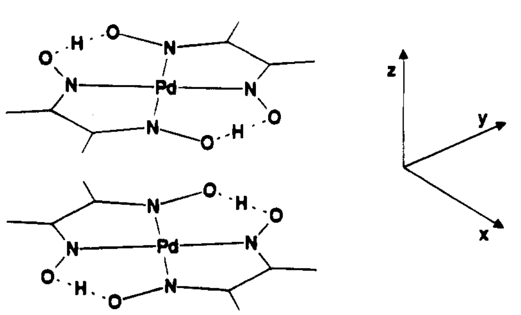


Figure 1. Geometry of the model $[Pd(gly)_2]_2$ cofacial dimer.

This paper reports the results of the first relativistic effective core potential (RECP) ab initio calculations on stacked palladium glyoximate oligomers. The description of the peculiarities of the valence band, the use of "the ion state formalism" as an extreme simulation of the partial oxidation process, and the variation of the valence bandwidth with interplanar geometries have been analyzed with the goal of understanding the electronic structure as well as bandwidth effects on the electrical conductivity of these materials. This work builds upon ab initio and first-principles DVM–Xα electronic structure calculations along with correlated He I/He II UV PE spectroscopy that we have previously carried out on the monomeric $Pd(gly)_2$ subunit.[20]

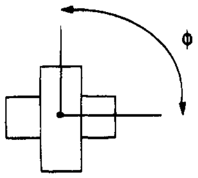
Computational Details

RECP ab initio calculations were carried out by using the restricted Hartree–Fock method for closed-shell states and the restricted open Hartree–Fock method for the open-shell states. The RECP's,[21] which explicitly treat the 10 valence electrons and the [2s,2p,2d] contraction basis set,[21] were adopted for the Pd atom. The standard all-electron 6-31G basis sets[22] were used for C, N, O, and H atoms.

The present calculations were performed on the model $[Pd(gly)_2]_2$ cofacial dimer (Figure 1). Metrical parameters for each monomeric subunit were taken from published diffraction data for $Pd(gly)_2I$[23] and $Pd(dpg)_2I$.[4] A series of conformations, including the observed 90° staggered equilibrium geometry[4,23] optimized to D_{2d} symmetry, eclipsed[24] (D_{2h} symmetry), and other staggered[24] (C_2 symmetry) conformations, were examined. Interplanar distances of 3.52 and 3.26 Å were used as found in the unoxidized and partially oxidized crystal structures, respectively. All calculations were performed using the HONDO8 program[25] on an IBM ES/9000 system.

Results and Discussion

Upon partial oxidation with iodine, $Pd(gly)_2$ and $Pd(dpg)_2$ form low-dimension stacked crystal structures having 90° staggered nearest neighbor conformations (**A**, $\phi = 90°$).[4,23] The



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oxidation is accompanied by a contraction in the metal–metal, interplanar stacking distance. Furthermore, it has been demonstrated that I_5^- is the predominant halide counterion species,[4,26] hence that the palladium glyoximate moieties bear formal +0.2 fractional charges ($Pd(dpg)_2{}^{0.20+}(I_5^-)_{0.20}$). Furthermore, partial oxidation of $Pd(dpg)_2$ is accompanied by alarge increase (ca. 10^7-10^8) in electrical conductivity in the macrocycle stacking direction ($\sigma||$). The conductivity of $Pd(dpg)_2I$ (four-probe single crystal measurements; $\sigma||(300) \sim (2-8) \times 10^{-5}\ \Omega^{-1}\ cm^{-1}$) is thermally activated (eq 1) with $\Delta = 0.39(2)$

$$\sigma|| = \sigma_0 e^{-\Delta/kT} \qquad (1)$$

eV over the temperature range 195–300 K. The corresponding values for $Ni(dpg)_2I$ are $(2.3-11) \times 10^{-3}\ \Omega^{-1}\ cm^{-1}$ and 0.22(2) eV.[27] The p-type thermopower of $Ni(dpg)_2I$ (20 μV/K at 300 K) argues that the charge transport is largely $Ni(dpg)_2{}^{0.2+}$-centered, rather than involving the polyhalide chains.[27] The similar charge transport characteristics of $Pd(dpg)_2Br_{1.1}$ (Br is present largely as Br_5^-) support this contention.[4b] Interestingly, the charge transport characteristics of $Ni(dpg)_2I$ (I is present largely as I_5^-) and $Ni(dpg)_2Br$ (Br is present largely as Br_5^-) are rather similar to those of the palladium analogues with the only difference being slightly greater conductivities in the nickel series.[4b]

Ab initio ground-state electronic structure calculations on monomeric $Pd(gly)_2$ (D_{2h} symmetry) have already been reported.[20] The highest, nearly degenerate, occupied molecular orbitals (MO's) are almost totally ligand-based and consist of the two symmetry combinations ($3b_{3g}$ and $2a_u$) of the $\pi_4{}^{20}$ ligand MO (Figure 2). A strong admixture with the $4d_{z^2}$ metal subshell is found in the $12a_g$ MO which lies 2.22 eV below the aforementioned ligand-based MO's.

The solid state condensation of the $Pd(dpg)_2$ molecules into stacks causes each electronic state to broaden into a band, the width of which becomes crucial for charge transport properties. Orbital energies of dimeric $[Pd(gly)_2]_2$ molecules in a 90° staggered cofacial orientation are shown in Figure 3. In the D_{2d} dimer with the same 3.52 Å Pd–Pd interplanar distance as found in the unoxidized crystals, the highest occupied MO's ($11b_1$, 25e, $11a_2$) remain ligand-based, π_4 in character. The HOMO–HOMO splitting E ($11b_1-11a_2$) ($2t$)[28] is 0.19 eV. This value implies a tight-binding bandwidth of $4t = 0.38$ eV for infinite stacks. Still in D_{2d} symmetry, a smaller 3.26 Å Pd–Pd interplanar spacing, as found in partially oxidized crystals,[4] results in an increased HOMO–HOMO splitting of 0.30 eV due to increased inter-HOMO overlap. The corresponding tight-binding bandwidth $4t$ would then be 0.60 eV.

Within a simple rigid band structure picture, it can be assumed that partial oxidation results in the depletion of electrons from the band nearest the Fermi level.[10] Therefore, the increased electrical conductivity of the partially oxidized glyoximate polymers depends upon partial depopulation of the uppermost band as well as upon the larger bandwidth[10] due, in turn, to the smaller interplanar spacing. The partial filling of the band does not, however, produce metal-like conductivity because the relatively narrow valence bandwidth may favor localized hole states either to minimize electron–electron repulsion[29] or to minimize the energies of polaron-like structures. These arguments are entirely consistent with static magnetic susceptibility measurements on $Ni(dpg)_2I$ and $Pd(dpg)_2I$[27] which indicate essentially complete spin localization (spin concentrations of 0.20 ± 0.02 and 0.17 ± 0.02 spins, respectively, per macrocycle) with a "Curie-like" behavior over a 5–300 K temperature range.[27]

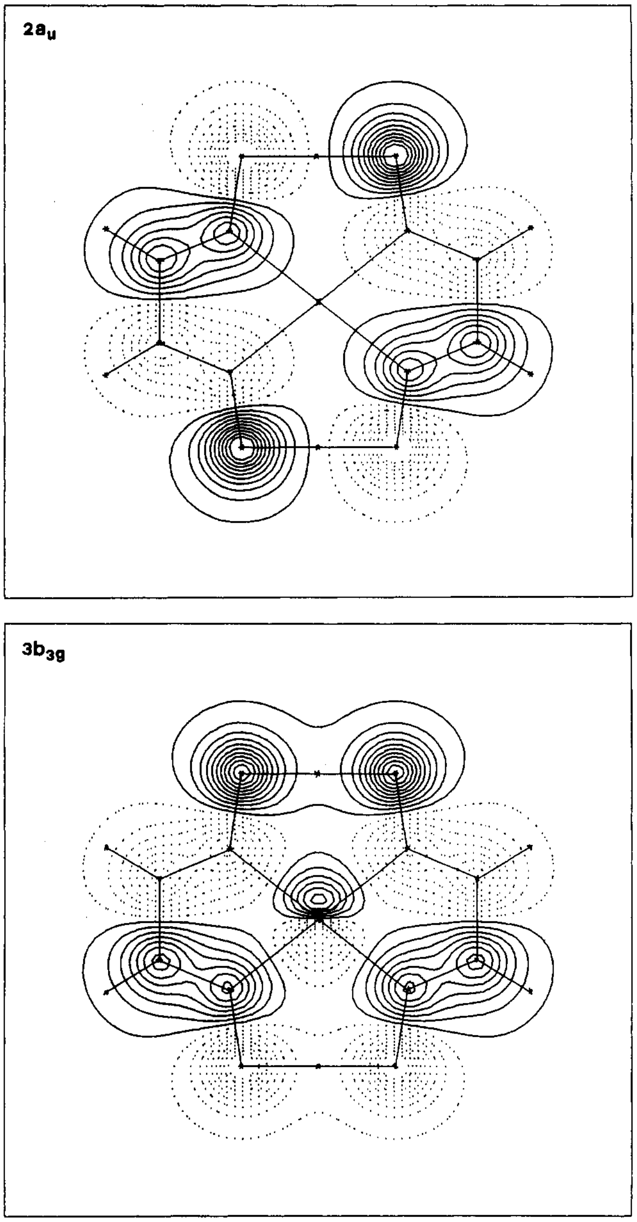

Figure 2. Wavefunction contour plots for the highest occupied $3b_{3g}$ and $2a_u$ MO's of the monomeric $Pd(gly)_2$ molecule shown 1.0 au above the molecular plane. The first solid and point contours are $\pm 0.133\ e^{1/2}/au^{3/2}$, respectively, and the interval between successive contours is 0.014 $e^{1/2}/au^{3/2}$. The dotted areas refer to the negative part of the wave function.

Band structure effects on the conduction process involve an additional consideration. Partial electronic depletion of the uppermost band undoubtedly causes reorganization of the electronic structure. Within a localized states description, the partial oxidation can be physically described in terms of creating open-shell states by depletion of electrons from the particular band involved in the process.[29] This means that the effects of partial oxidation upon the ground-state system can be reasonably extrapolated from those due to electronic reorganization[17] in the ionization processes of the dimer (neglecting vibronic coupling effects). Table 1 reports energies associated with final states produced upon unit electron removal from some of the upper-

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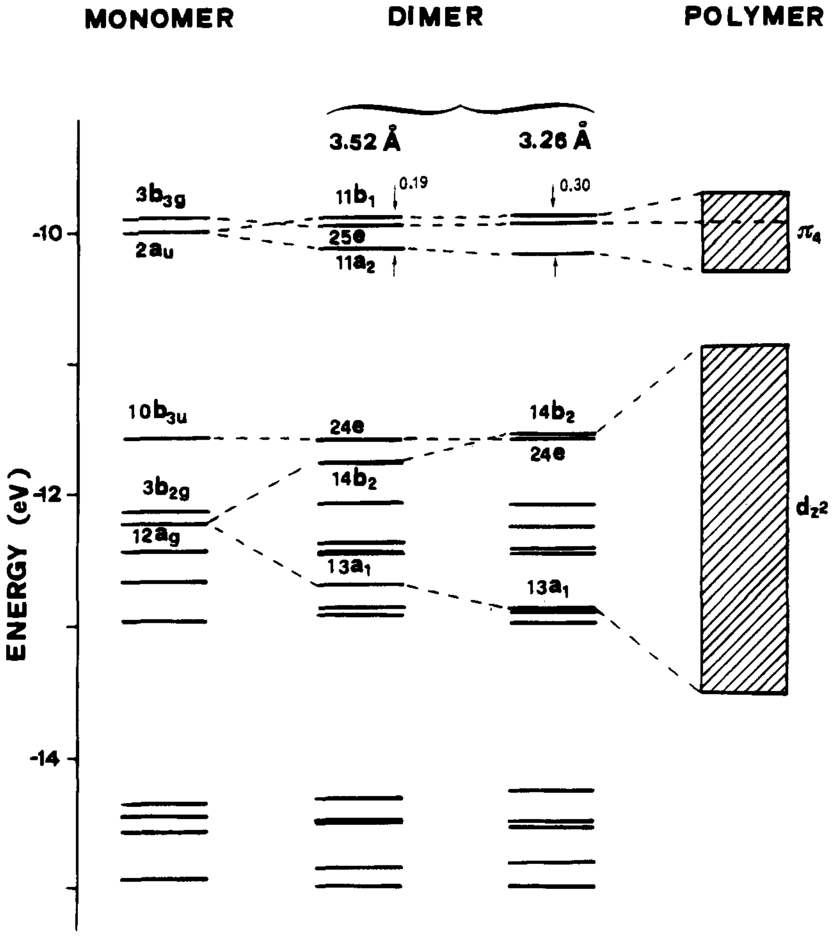

Figure 3. Molecular orbital energy diagram for the monomeric $Pd(gly)_2$ molecule and for the 90° staggered cofacial $[Pd(gly)_2]_2$ dimer at two different interplanar separations. Tight-binding bandwidths (4*t*) extrapolated to the $[Pd(gly)_2]_n$ polymer are also shown.

Table 1. Eigenvalues and Computed IE's (eV) of the Uppermost MO's of the $[Pd(gly)_2]_2$ Dimer (Interplanar Distance = 3.26 Å)

MO	$-\epsilon$	IE	dominant character
$11b_1$	9.89	9.61	π_4
25e	9.94		π_4
$11a_2$	10.19	9.91	π_4
$14b_2$	11.56	10.01	d_{z^2}

most MO's of the $[Pd(gly)_2]_2$ dimer.[30] These energies, the ΔSCF ionization energies (IE's), although sizable are not sufficiently large in the case of the $14b_2$ (d_{z^2}) MO to reorder the energy sequence of the ground-state orbitals near the Fermi level. Moreover, since these energies represent the upper limits for energy shifts in the partially oxidized chain, it can be safely argued that in the partially oxidized glyoximate polymer, having a +0.2 formal charge on each metal glyoximate moiety, the band associated with the d_{z^2} orbital remains below the Fermi level.

Taken together, these observations suggest that the $2a_u$ (π_4)-derived valence band represents the major pathway for charge transport in the equilibrium conformation of the partially oxidized polymer.[31] This agrees well with the aforementioned, minimal dependence of the electrical conductivity upon the nature of the central metal atom in partially oxidized nickel and palladium bis(glyoximate) complexes.[4,32]

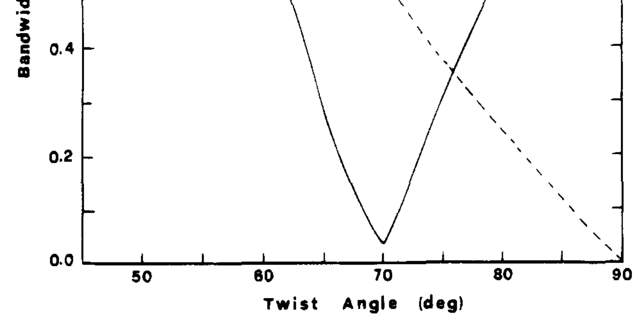

Figure 4. Variation of the calculated $2a_u$ (solid line) and $3b_{3g}$ (dashed lines) valence bandwidths with twist angle in the $[Pd(gly)_2]_2$ dimer (interplanar separation = 3.26 Å).

The thermally activated behavior of the electrical conductivity[4] in the subject compounds requires additional comment.

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[30] Note that the ΔSCF values are quite close to Koopmans' IE's, suggesting only minor electron reorganization following ionization, as is reasonable for these delocalized molecules.

[31] These and the following considerations are of course only valid assuming that the valence band structure remains essentially unchanged on passing from $[Pd(gly)_2]_n$ to $[Pd(dpg)_2]_n$.

[32] Band structure calculations on $[Ni(gly)_2]_n$[17,18] arrived at exactly the same conclusion.

Relatively narrow bandwidths (<1.0 eV) may favor localization to form polaron carriers, due to strong coupling of conduction electrons to intramolecular phonons as well as to intermolecular phonons and librations. This produces an entirely different thermal dependence of charge transport than is seen in typical "molecular metals" where a $\sigma \sim T^{-n}$.[2,7,15b,33] Figure 4 depicts the dependence of the bandwidths ($4t$) of the $2a_u$ and $3b_{3g}$ relatedMO's of the model dimer upon the twisting angle, which describes the mutual staggering angle between the cofacial $Pd(dpg)_2$ units in the $[Pd(dpg)_2]_2$ dimer (**A**; 90° = the equilibrium geometry). Two bandwidth maxima are found at $\phi = 45°$ and $\phi = 90°$. The smallest bandwidths (and lowest calculated total energy) are found for a $\phi = 70°$ staggering angle. More interesting, the reduced symmetry in the $\phi < 90°$ conformations causes the $3b_{3g}$ band, of zero width in the staggered ($\phi = 90°$) conformation due to the degeneracy of $3b_{3g}$-derived 25e levels, to broaden due to removal of the degeneracy ($e \rightarrow 2{\cdot}b$). This effect may be of relevance to the charge transport.

Interestingly, the band structure results suggest that near $\phi = 50°$, both the larger bandwidths and smaller variation of bandwidth with librational amplitude may give rise to the metal-like behavior characteristic of a true "molecular metal". Such a conductivity characteristic must occur at relatively high temperature, with semiconductivity at lower temperature. This is reminiscent of situations involving Peierls distortions, but here the localization at low temperature is suggested to be direct librational, not translational, modulation of the transfer integral. There is thus a fairly straightforward but interesting generalization of the simple Mott–Peierls localization and transition behavior brought about by the planar, π-type localized MO's on each metallomacrocycle that act as the sites defining the tight-binding bands. The extra degree of freedom arising from libration provides both a more sensitive temperature dependence of the conductivity[14–18] and a large enough reduction in the effective bandwidth to yield low-temperature semiconductive behavior. All platelike, stacked organic conductors should be expected to show, to differing extents, this extra modulation beyond that, due to longitudinal phonons, which always occurs in any one-dimensional chain.

Conclusions

Despite the limitations of a simple cluster approach and of the tight binding approximation, the use of ab initio calculations has provided valuable information on the composition of the valence band of low-dimensional conducting metal glyoximate materials. Thus, it has been found that the bands near the Fermi level are built up from near-degenerate ligand-centered $3b_{3g}$ and $2a_u$ π_4 MO's. These are totally ligand-based. Metal-like conductivity has not been observed in partially oxidized crystals of bis(glyoximate) metallomacrocycles, either because the Hubbard on-site Coulomb repulsion (U term) remains large enough in comparison to the bandwidth ($4t$) to favor localized states ($t \ll U/4$)[29] or because the narrow bandwidth gives rise to polaron-type (localized) charge carriers due to vibronic interactions.

Finally, differences in charge transport properties found in partially oxidized phthalocyanines[7,8] and glyoximates[4,5] cannot be explained simply in terms of differences in the composition of the valence band.[18] It appears that both larger bandwidths[7,14,15] and spreading of electron densities[14,15] (hence smaller U term) lead to metal-like behavior in the phthalocyanines. Libron scattering results in a negative influence on conductivity since it reduces bandwidth.[14,15a] By contrast, in $Pd(gly)_2I$ the smaller bandwidths, larger U values, and vibronic coupling lead to a semiconducting behavior.

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