

Structural and Spectroscopic Properties of One-Dimensional  
Platinum Chain Compounds

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A material is defined as one-dimensional (1-D) if there exists a "gross" anisotropy in at least one intensive property [1]. For one-dimensional metals, conductivity is the anisotropic property of concern.

Highly conducting 1-D inorganic compounds are mainly restricted to partially oxidized tetracyanoplatinates (TCP) and bis(oxalato)platينات (M-OP) for chemical and structural reasons [2]. Square planar environment for metals and small non-bulky ligands favor complex stacking such that the overlap of the  $d_{z^2}$  orbital on adjacent metals is maximized [3].

The intense interest in the 1-D platinate salts is in part due to Little's observation that 1-D metals may exhibit excitonic superconductivity at elevated temperatures [4]. Additionally, these compounds provide real examples of theoretical, low dimensional models [5].

The electronic properties of partially oxidized TCP's or M-OP's can best be modelled by modified free electron band theory [6]. Peierls predicted that a 1-D metal would be unstable to a coupled electron phonon distortion that spanned the Fermi surface [7]. The metal-insulator transition in 1-D compounds is understood as a manifestation of the Peierls distortion, which is analogous to the Jahn-Teller distortion in transition metal chemistry [1b].

Interchain coupling establishes a three-dimensional ordering or phase transition at a finite temperature,  $T_{3D}$ , at which the cooperative interchain forces become significant compared to the thermal energy. These cooperative forces are dependent on amount of hydrogen bonding [8] and counter ion polarizability [9]. Commensurate cation ordering with the lattice in divalent bis(oxalato)platينات cause the formation of non-Peierls superstructures [10]. The phase transition associated with cation ordering thwarts the Peierls distortion in these compounds.

X-ray diffraction techniques are the most instrumental in characterizing the state and transition between states for 1-D metals [11]. Diffuse layers bracketing the Bragg reflections are indicative of one-dimensional Peierls ordering [12]. The position of these diffuse layers with respect to the Bragg reflections is the most accurate measure of the degree of partial oxidation [12]. The collapse of the diffuse layers into discrete reflections indicates a three-dimensional ordering phase transition [13]. The presence of reflections other than Bragg reflections means that non-Peierls superstructure exists [10].

The electron transport properties, which are the major concern of partially oxidized TCP's and M-OP's, depend on: mode and degree of partial oxidation; size and polarizability of counter ions; crystalline environment of the metal conduction spine; interchain coupling; and the type of superstructure formation [1]. All of these properties are interrelated and thus it is difficult to isolate the effect of one property on the conductivity. However, isostructural compounds, in which variations of counter ion, degree of partial oxidation, and

interchain coupling can be engineered, provide glimpses into their isolated effects on conductivity. This allows generalization of trends and knowledge of the important factors leading to one dimensional conductivity.

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