

## Synthetic Metals: Structural Control of Electronic Properties

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A variety of molecular systems in the solid state exhibit the electrical, optical and magnetic properties of metals. Three systems of particular interest to the inorganic chemist are: (1) partially oxidized platinum complexes; (2) metallomacrocycles; and (3) chalcogen network compounds. These systems can be chemically modified in terms of structure, degree of partial oxidation (DPO), counterions, etc., and the effects of these modifications on physical properties lead to a clearer understanding of the metallic state. Other goals of synthetic metal synthesis include retention of metallic behavior at low temperatures and room temperature superconductivity [1,2].

Among the first synthetic metals were stacked  $\text{Pt}(\text{CN})_4^{2-}$  units, forming a large family of partially oxidized tetracyanoplatinate salts (POTCP) initially derived from  $\text{K}_2[\text{Pt}(\text{CN})_4]\text{Br}_{0.30} \cdot 3\text{H}_2\text{O}$ , Krogmann's salt  $[\text{KCP}(\text{Br})]$  [3]. The POTCP salts were followed by tetrathiafulvalene-tetracyanoquinone (TTF-TCNQ) [4], the first highly conducting ( $\sigma_{\text{RT}} \approx 200 \Omega^{-1}\text{cm}^{-1}$ ) organic solid. These two systems typify synthetic metals. They consist of closely spaced planar units forming segregated stacks in which intermolecular orbital overlap gives rise to energy bands along the stacking axis. As conduction can then easily occur only along the stacking axis, these compounds exhibit highly anisotropic conductivities;  $\sigma_{\parallel}/\sigma_{\perp}$  can be as high as  $10^5$  [5].

Due to this quasi-one-dimensionality, these compounds are electronically unstable with respect to a variety of one-dimensional to three-dimensional transitions. The Peierls distortion [6] refers to a permanent periodic lattice distortion that opens up a gap in the energy band structure. X-ray diffraction is then clearly a powerful tool in observing Peierls transitions. This phase transition is similar to the Jahn-Teller distortion in molecules in that filled electron states are lowered in energy and unfilled states raised.

The effect of structural changes on conductivity has been studied in seventeen well-characterized POTCP salts,  $\text{M}_x[\text{Pt}(\text{CN})_4]\text{X}_y \cdot n\text{H}_2\text{O}$ , which form a family of compounds with varying Pt-Pt distances ( $d_{\text{Pt-Pt}}$ ) [5,9-12]. All of these compounds exhibit modulated structures due to Peierls distortions. The complexes vary with regard to DPO, Peierls band gap ( $\Delta$ ), three-dimensional ordering temperature ( $T_{3D}$ ) and the theoretically derived interchain coupling ( $\eta$ ) and electron-phonon coupling ( $\lambda$ ) parameters. All of these parameters can be correlated with  $d_{\text{Pt-Pt}}$ , and the correlations can be understood in terms of changes in the energy band structure with varying Pt-Pt distances.

The metallomacrocycles [14-17], studied primarily by Marks, Hoffman, and Ibers, form another chemically variable system. The best understood system is the phthalocyanines (Pc). Nickel phthalocyanine [18],  $[\text{NiC}_{32}\text{H}_{16}\text{N}_8]$ ,  $\text{Ni}(\text{Pc})$ , crystallizes in a stacked structure of planar rings, which when oxidized by iodine, becomes a synthetic metal ( $\sigma_{\text{RT}} = 500 \Omega^{-1}\text{cm}^{-1}$ ).  $\text{Ni}(\text{Pc})\text{I}$  exhibits metallic properties to below 2 K; this absence of any metal-insulator transition is due to

the presence of disordered  $I_3^-$  chains and the lack of significant interstack interactions. As Ni(Pc) charge-transfer complexes proved to be integrated stack insulators, attempts to control stacking architecture resulted in the synthesis of cofacially-linked Pc polymers,  $[M(Pc)O]_n$  [19,20]. Variation of the ring center species, M, leads to variation of the Pc-Pc interplanar spacing ( $d_{Pc-Pc}$ ). Increasing  $d_{Pc-Pc}$  (Ni < Si < Ge) decreases the conductivity, increases the Pauli-like magnetic susceptibility ( $\chi$ ) and decreases the optical reflectivity frequency ( $\omega$ ), all indicating a structurally correlated decrease in bandwidth.

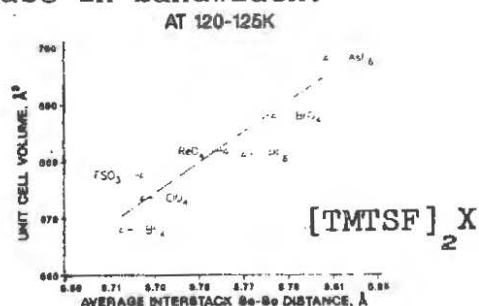


Figure 1

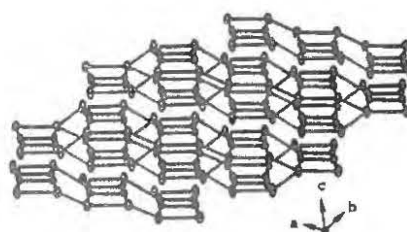


Figure 2

The discovery of pressure-induced superconductivity in  $(TMTSF)_2PF_6$  [21] (TMTSF = tetramethyltetraselenofulvalene) led to a variety of  $(TMTSF)_2X$  [22,22] compounds, culminating in  $(TMTSF)_2ClO_4$  [24], an ambient-pressure superconductor with  $T_C = 1.1$  K. The structures of these  $(TMTSF)_2X$  salts indicate formation of a three-dimensional network [25] of selenium atoms, the TMTSF conduction pathway. Recent x-ray diffraction studies produced a correlation between anion size and Se-Se distances [26] ( $d_{Se-Se}$ ) with minimum  $d_{Se-Se}$  centering around  $(TMTSF)_2ClO_4$  (Figure 1). From this correlation, unit cell volume and thus, Se-Se distances, can be predicted from anionic size. Two other ambient pressure superconductors are based on BEDT-TTF [23, 25,27] (bisethylenedithiotetrathiafulvalene):  $(BEDT-TTF)I_3$  [28] and  $(BEDT-TTF)IBr_2$  [29]. Unexpectedly the S-S intrastack interactions are significantly weaker than the interstack interactions leading to formation of an infinite two-dimensional sulfur atom network (Figure 2). Changing the  $I_3^-$  anion to the shorter (~7%)  $IBr_2^-$  anion, results in a contraction of the S-S network and an increase in the superconductivity onset temperature ( $T_C$ ), from 1.4 K to 2.7 K. Such chalcogen network superconductors are very different from the majority of synthetic metals as they are not one-dimensional. Hopes to further raise  $T_C$  center on tellurium-based compounds

Clearly, from a synthetic chemical standpoint, the ability to tailor charge-transporting microstructures at the atomic level represents both an exciting challenge and a key to manipulating macroscopic properties and to testing theoretical predications. In the future, new synthetic systems will lead to a greater understanding of the complex interrelationships between structure and electronic properties.

## References

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