

TCNQ SALTS OF PLANAR METAL COMPLEX CATIONS: NOVEL MOLECULAR CONDUCTORS AND SEMICONDUCTORS.

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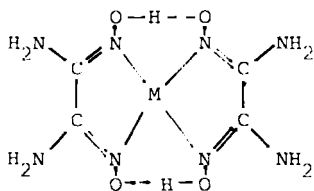
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Abstract The facile variation of positive charge of oxamide oxime metal complexes, caused by acid-base equilibrium, allows the growth of single crystals of their TCNQ⁻ salts. 1:1 salts consist of regular segregated stacks of the components, with metallic room temperature behaviour of the Ni compound, the Pt compound being a semiconductor. Room temperature conductivities are of the order of 10 Siemens per cm. A 2:3 Pt complex TCNQ salt contains segregated acceptor stacks with half a negative charge per molecule. These stacks run perpendicular to mixed stacks -D-D-A-D-D-A-, with integral charges on donors D and acceptors A.

INTRODUCTION

As a function of pH, the neutral bis(oxamide oximato)metal complexes of Ni(II), Pd(II), Pt(II), $[M(oaoH)_2]^0$, accept reversibly



one or two protons to yield monoprotonated or diprotonated cations. From the ions $[Ni(oaoH_2)_3]^{2+}$ and $[M(oaoH_2)_2]^{2+}$, M=Pd, Pt, the salts $[M(oaoH)(oaoH_2)]^+ TCNQ^-$, M=Ni, Pd, Pt are obtained.¹ During

crystal growth of the Pt compound, the 2:3 salts $2[\text{Pt}(\text{oaoH})(\text{oaoH}_2)]^+(\text{TCNQ})_3^{2-}$ forms as a by-product.

STRUCTURES AND PROPERTIES

The three 1:1 salts with $M=\text{Ni}, \text{Pt}, \text{Pd}$ are isomorphous. Crystals consist of segregated regular stacks of cations and anions (Figure 1). This structure is stabilized by H bridges between adjacent cations, and between cations and anions. The 2:3 salt exhibits the unusual feature of a $(\text{TCNQ})^{-1/2}$ stack perpendicular to a -D-D-A-D-D-A- stack, with integral charges on donors and acceptors (Figure 2).

As expected for a single valent TCNQ^- salt, D.C. conductivity and thermopower of the 1:1 Pt salt indicate semiconducting behaviour, $\sigma_{RT} \approx 5 \Omega^{-1}\text{cm}^{-1}$. Surprisingly, the Ni salt has a metallic regime at room temperature, $\sigma \approx 15 \Omega^{-1}\text{cm}^{-1}$. D.C. conductivity, thermopower, and EPR measurements (Figure 3) indicate a metal to semiconductor phase transition around 230K, but in the microwave conductivity the transition shows up around 170K (Figure 4).

CONCLUSIONS

The different behaviour of the Pt and Ni 1:1 salts hints at a mixed valence character of the latter one, caused by TCNQ^0 doped into the TCNQ^- stack. The lack of negative charge may be compensated by proton vacancies in the metal complex stacks (raising the question of possible proton conductivity along these stacks). That TCNQ^- is partially oxidized to TCNQ^0 during the crystal growth is evident by the formation of the 2:3 Pt salt. If the mixed valence character of the Ni salt can be confirmed, there is a chance to prepare solids with adjustable band filling without implying redox processes: The average charge per complex species may be controlled by the pH of the solution, and the $\text{TCNQ}^-/\text{TCNQ}^0$ ratio is easily varied by working with $\text{LiTCNQ}/\text{TCNQ}$ mixtures.

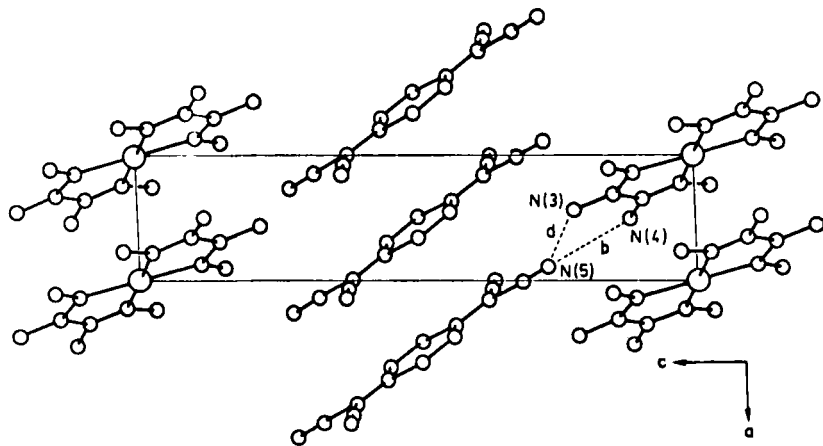


FIGURE 1 Structure of the 1:1 salts projected perpendicular to the stacks.

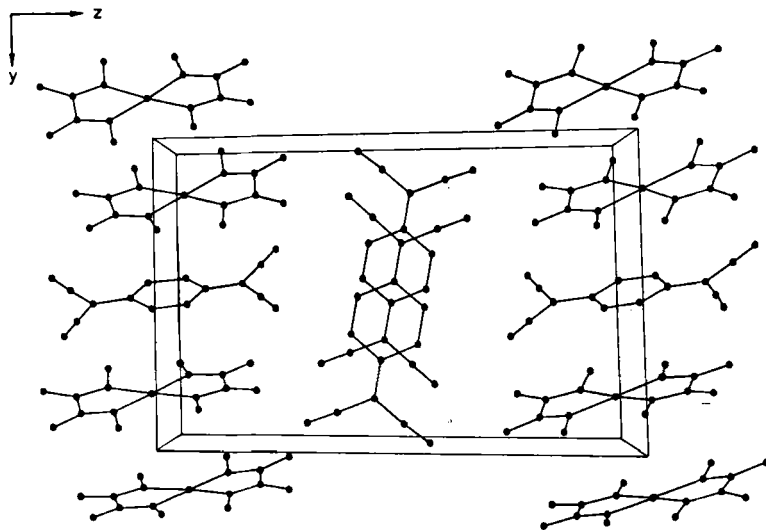


FIGURE 2 Structure of the 2:3 Pt salt projected along the TCNQ stack.

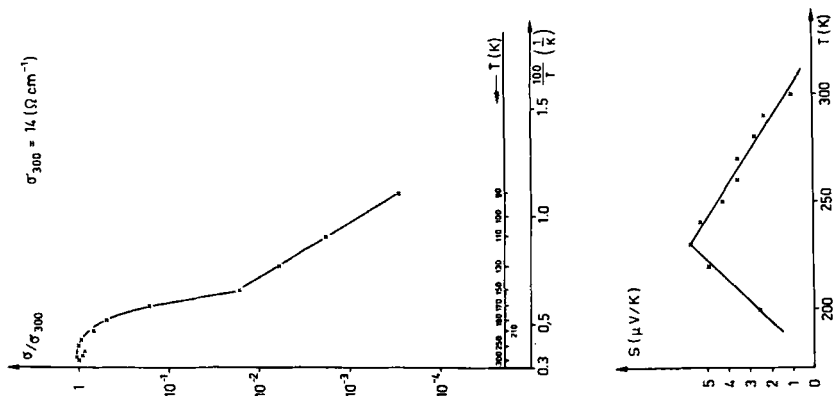


FIGURE 3 D.C. conductivity (left) and thermopower (right) of $[\text{Ni}(\text{oaoH})(\text{oaoH}_2)]\text{TCNQ}$.

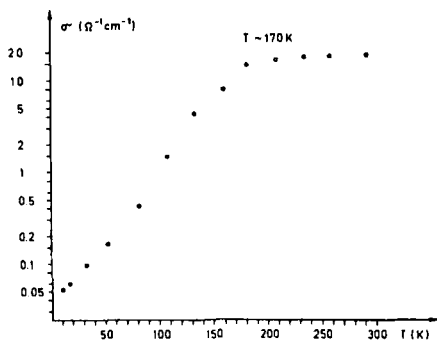


FIGURE 4 Microwave conductivity of the 1:1 Ni salt.

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