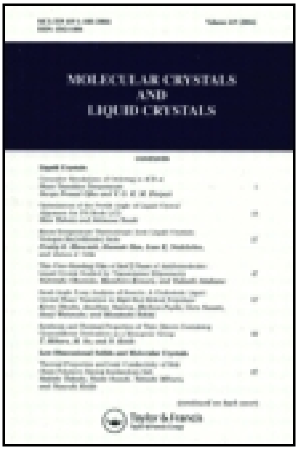


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

TCNQ Salts of Planar Metal Complex Cations: Novel Molecular Conductors and Semiconductors

Helmut Endres [a], August Bongart [a], Dietrich Nöthe [a], Ingolf Hennig [b], Dieter Schweitzer [b], H. W. Helherg [c] & H. Schäfer [c]

[a] Anorg. Chem. Institut der Universität, D-6900, Heidelberg, 1, FRG
[b] MPI f. Med. Forschung, Abt. Molekulare Physik, D-6900, Heidelberg, 1, FRG
[c] III. Physik. Institut dor Universitat, D-3400, Göttingen, FRG

Version of record first published: 17 Oct 2011.

To cite this article: Helmut Endres , August Bongart , Dietrich Nöthe , Ingolf Hennig , Dieter Schweitzer , H. W. Helherg & H. Schäfer (1985): TCNQ Salts of Planar Metal Complex Cations: Novel Molecular Conductors and Semiconductors, Molecular Crystals and Liquid Crystals, 120:1, 365-368

To link to this article: http://dx.doi.org/10.1080/00268948508075821

Mol. Cryst. Liq. Cryst. 1985, Vol. 120, pp. 365-368
0026-8941/85/1204-0365/$10.00/0

Printed in the United States of America

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

HELMUT ENDRES, AUGUST BONGART, DIETRICH NÖTHE
Anorg.Chem.Institut der Universität, D-6900 Heidelberg 1, FRG.

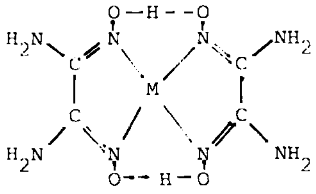
INGOLF HENNIG, DIETER SCHWEITZER
MPI f.Med.Forschung, Abt.Molekulare Physik, D-6900 Heidelberg 1, FRG.

H.W. HELBERG, H. Schäfer
III.Physik.Institut der Universität, D-3400 Göttingen, FRG.

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), $[M(oaoH)_2]$, accept reversibly



one or two protons to yield monopositive or dipositive 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 $2[Pt(oaoH)(oaoH_2)]^+(TCNQ)_3^{2-}$ forms as a by-product.

STRUCTURES AND PROPERTIES

The three 1:1 salts with M=Ni, Pt, 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 $(TCNQ)^{-1/2}$ 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, $\sigma RT \approx 5\ \Omega^{-1}cm^{-1}$. Surprisingly, the Ni salt has a metallic regime at room temperature, $\sigma \approx 15\ \Omega^{-1}cm^{-1}$. 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 $TCNQ^o$ 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 $TCNQ^o$ 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 $TCNQ^-/TCNQ^o$ ratio is easily varied by working with LiTCNQ/TCNQ mixtures.

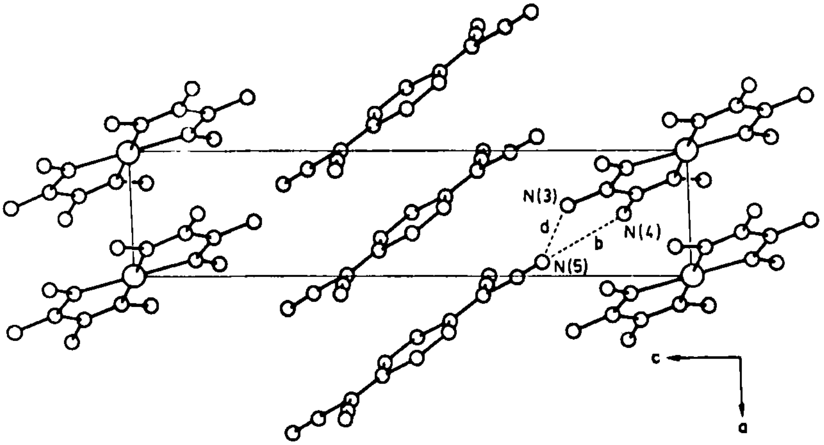


FIGURE 1 Structure of the 1:1 salts projected perpendicular to the stacks.

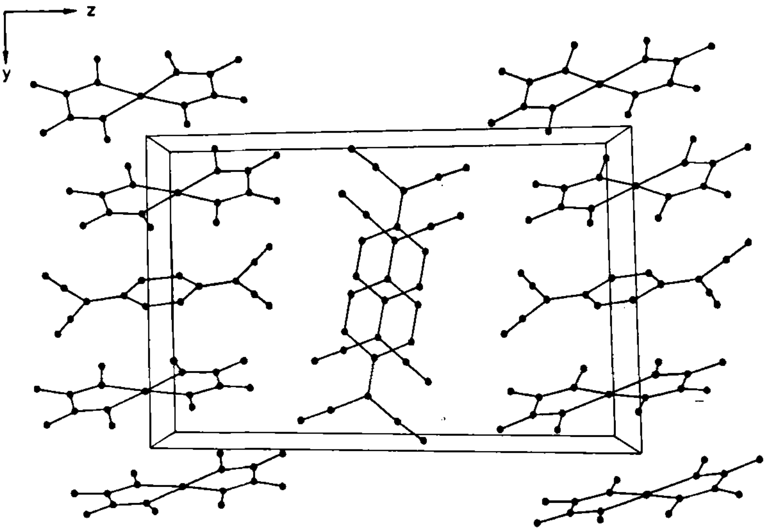


FIGURE 2 Structure of the 2:3 Pt salt projected along the TCNQ stack.

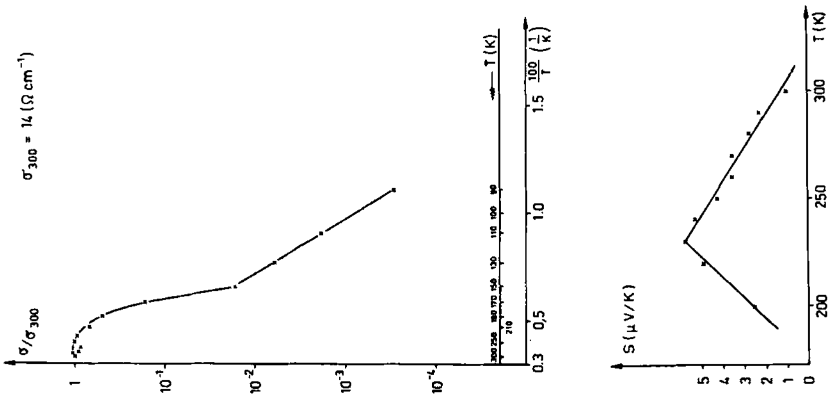


FIGURE 3 D.C. conductivity (left) and thermopower (right) of $[Ni(oaoH)(oaoH_2)]TCNQ$.

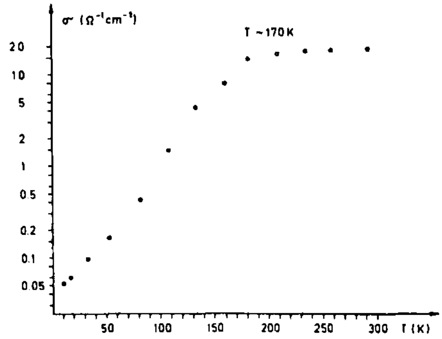


FIGURE 4
Microwave conductivity of the 1:1 Ni salt.

ACKNOWLEDGEMENTS

This work is made possible by a grant from Stiftung Volkswagenwerk. Support from Fonds der Chemischen Industrie and donations of Pd and Pt salts by DEGUSSA, Hanau (FRG) are also gratefully acknowledged.

REFERENCES

1. H. Endres, Angew.Chem.Intern.Edition, 21, 524 (1982), Angew.Chem.Suppl., 1309 (1982).