

Counter-ion influences on the electrical conduction properties of 1,2-dithiolene coordination compounds

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COUNTER-ION INFLUENCES ON THE ELECTRICAL CONDUCTION PROPERTIES OF
1,2-DITHIOLENE COORDINATION COMPOUNDS

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INTRODUCTION

The intention of the present study is to investigate the coordination chemistry and the magnetic and conducting properties of polynuclear coordination compounds containing 1,2-dithioleenes. DMIT-based ($H_2DMIT = 4,5$ -dimercapto-1,3-dithiol-2-thione) complexes have become of particular interest since the discovery of superconductivity in $(TTF)[Ni(DMIT)_2]_2^{1}$. With DMIT and related ligands square planar compounds are obtained for $M = Ni, Cu, Pd$ and Pt , see Figure 1.

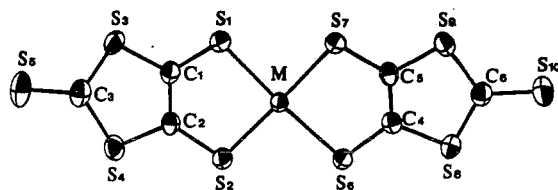
An important and general feature of the above-described compounds is the variety of apparent oxidation states for the metal ions, as well as the fact that these can easily be converted into each other.

RESULTS, DISCUSSION AND CONCLUSIONS

The compound $(Et_4N)_1[Ni(DMIT)_2]$, prepared by oxidation by iodine of $(Et_4N)_2[Ni(DMIT)_2]^{2,3}$, crystallizes in the space group $P2_1/n$, its structure has been solved by X-ray diffraction methods. See Figure 1. for crystallographic parameters and distances. It is a zig-zag chain with the shortest intermolecular distances 3.8 \AA .

Oxidation of $(Et_4N)_2 Pd(DMIT)_2$ with air afforded crystals of $(Et_4N)_{0.5} [Pd(DMIT)_2]$, of which the crystal structure was solved as well. Its structural parameters are tabulated in Figure 1. This compound is a two-dimensional S...S network with nearest S...S contacts in the range of 3.26 to 3.72 \AA .

Both compounds are semiconductors with a linear behaviour of $\ln \sigma$ vs. $1/\sqrt{T}$, see Figure 2. From the single crystal conductivity measurements of several compounds with DMIT can be concluded that the conductivity is strongly dependent on the cation, as well as on the metal atom and its oxidation state (Figure 3).



	$[(C_2H_5)_4N]_1Ni(DMIT)_2$	$[(C_2H_5)_4N]_{0.5}Pd(DMIT)_2$
Space group	$P 2_1/n$	$P \bar{1}$
a, Å	7.333(1)	18.873(6)
b, Å	25.734(3)	8.515(3)
c, Å	12.798(4)	6.295(2)
α , (°)	90.0	117.77(9)
β , (°)	104.95(2)	96.66(3)
γ , (°)	90.0	90.78(3)
Z	4	2
R/R _w	4.49/5.36	2.89/2.97
M-S1, Å	2.151(4)	2.294(1)
M-S2	2.158(4)	2.308(1)
M-S6	2.159(4)	2.292(1)
M-S7	2.163(4)	2.302(1)
C1-C2	1.34(1)	1.375(5)
C4-C5	1.36(1)	1.401(6)
S1-M-S2, (°)	93.3(1)	90.41(5)
S1-M-S7	87.1(1)	87.84(5)
S2-M-S6	86.0(1)	91.44(5)
S6-M-S7	93.8(2)	90.07(5)

Fig. 1. Molecular structure and structural parameters of $(Et_4N)_1 Ni(DMIT)_2$ and $(Et_4N)_{0.5} Pd(DMIT)_2$.

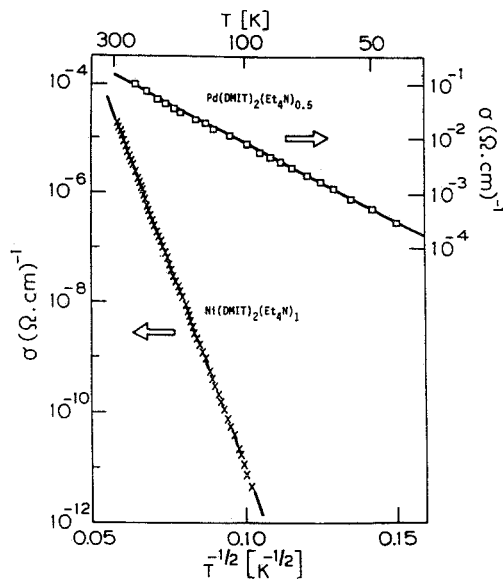


Fig. 2. Conductivity of $(Et_4N)_1[Ni(DMIT)_2]$ and $(Et_4N)_{0.5}[Pd(DMIT)_2]$ vs. $1/\sqrt{T}$.

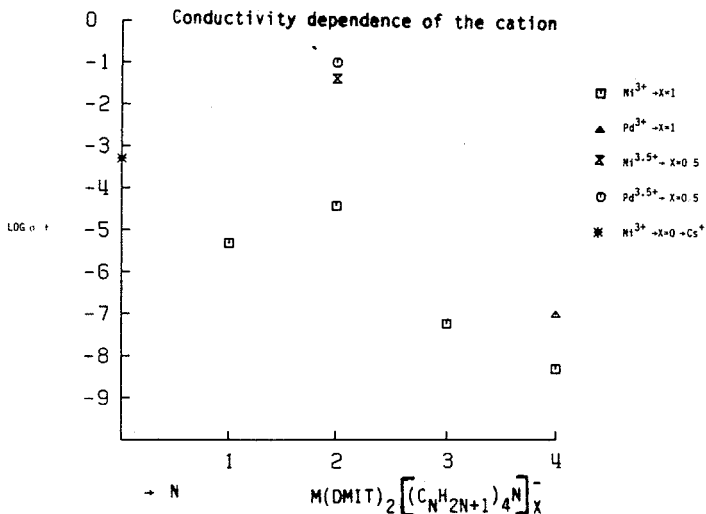


Fig. 3. Conductivity dependence on the cation of $(cat)_x[M(DMIT)_2]$. For $Ni^{3.5+}$ see ref. 4.

The magnetic measurements of the Ni and Pd compounds indicate 1-D behaviour and possibly a small trace of impurities. 1H -NMR reveals that at low temperature molecular motion of the tetraethylammonium group is still present (Figure 4). This is of particular importance, since the anomalous conductivity behaviour is in general an indication of disorder. In the present compounds disorder may be caused by cationic motion. Because linewidth studies reveal that two cation conformations occur, static disorder might be expected at the lowest temperature.

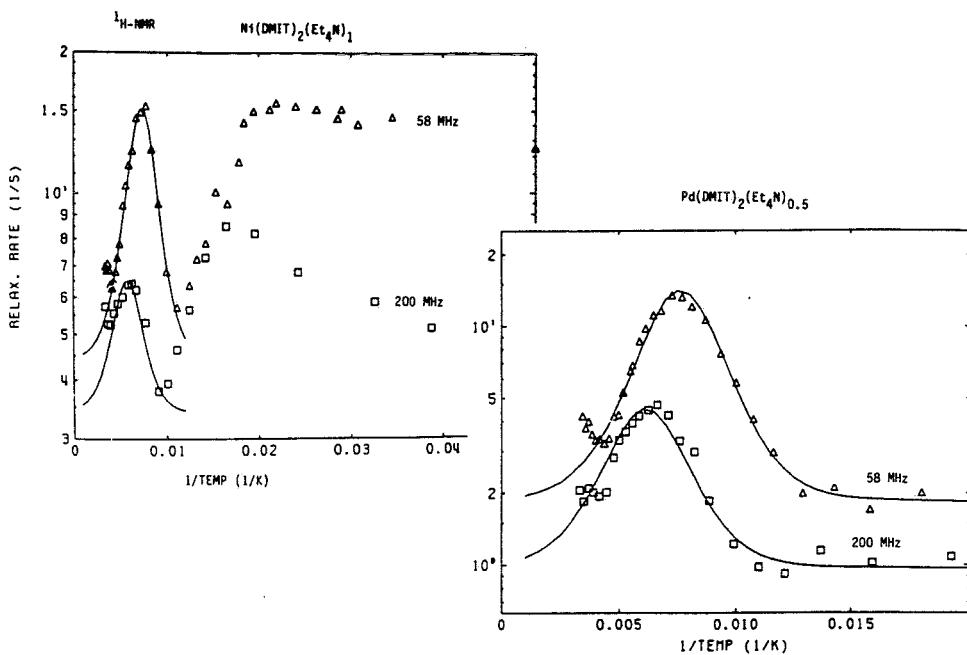


Fig. 4. Proton NMR relaxation rates vs. $1/T$ of $(Et_4N)_1[Ni(DMIT)_2]$ and $(Et_4N)_{0.5}Pd(DMIT)_2$

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