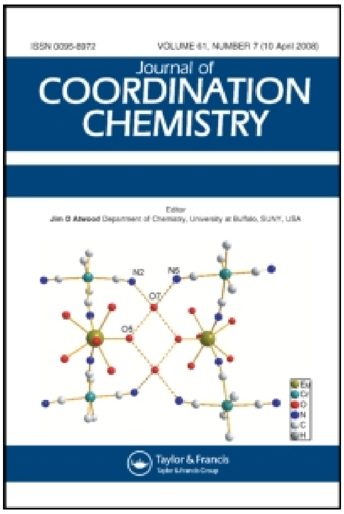

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ELECTRICAL PROPERTIES OF $M(S_2C_2(CN)_2)_2^{1-}$(M = Ni, Pt) COMPLEXES

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Single crystal conductivity studies over a temperature range of 200°K to 400°K have been carried out on various $M(S_2C_2(CN)_2)_2^{1-}$ (M=Ni,Pt) salts. A room temperature conductivity of $\sim 10^{-10}\,ohm^{-1}\,cm^{-1}$ and an $E_a \cong 0.5$ eV was observed for each of these systems. These results are correlated with the magnetic, electronic, and crystallographic properties. The semiconducting behavior of these systems is related to the electronic structure of the molecular anion.

INTRODUCTION

In the past decade there has been heightened interest in the solid state properties of inorganic[1,2] and organic[1,3] systems due to the observation of high electrical conductivity and cooperative magnetic properties. The physical properties of these systems depend upon the intermolecular interactions in the solid state which are governed by the electronic and crystal structure of the materials. Systems with a noneven number of electrons per molecular moiety, close approach between molecules, and good π overlap between adjacent molecules, are of particular interest because of their potential for forming substances exhibiting unusual electrical and magnetic interactions.[2a,4,5] Such intermolecular overlap further requires a large extension of an orbital perpendicular to the molecular plane. For the transition metals, the $5d_{z^2}$ has the largest spatial extent and, hence, square planar third row transition metal complexes have been the inorganic coordination complexes most likely to form highly conducting one-dimensional materials.[6] In order to stabilize a highly conducting system the individual complexes should have delocalized charge to reduce the Coulomb repulsion and possess a high electron affinity so that a molecule can take on either one or two excess electrons.

Paramagnetic square planar bis-maleonitriledithiolate (mnt) complexes, $\underline{1}$, (M=Ni,Pt) satisfy these requirements as the complexes are small, planar, delocalize charge, and exhibit high electron affinity while possessing a noneven number of electrons.[7]

Several groups have investigated the electrical properties of neutral,[8-11] monoanionic,[8,11-19] and dianionic[11,15,16,21-23] dithiolene complexes. The electronic structures of the nickel triad neutral and dianionic dithiolene complexes results in either an empty or doubly occupied electron energy level. Thus, low conductivity (consistent with experiment) would be anticipated. In contrast to these neutral and dianionic dithiolene complexes the nickel triad monoanionic dithiolenes have an odd number of electrons. The resulting singly occupied orbital may form a half-filled electron energy band if a uniform 1-D chain were formed.

The crystal structure of $Ph_3MeP^+Ni(mnt)_2^-$, $\underline{2}$, shows that $Ni(mnt)_2^-$, $\underline{1}$, (M=Ni) forms isolated stacks with dimerization within each stack,[20] and interplanar spacings (alternately 3.412 Å and 3.555 Å) shorter than van der Waals.[8] There is no direct metal–metal overlap within the stacks, however, the $M(mnt)_2^-$ is the most promising of metal dithiolene systems[7] because of the relatively close stacking, even between dimers.

Typically square planar bis-dithiolene monoanionic complexes exhibit low conductivity.[8,11,13,15-18] High conductivity, however, has been reported for several salts containing charged organic radical cations which may provide the pathway for electrical transport.[11,12,14,15,22] Anomolously high conductivity has also been reported for compressed pellets of the hydrated ammonium salt of $Pd[S_2C_2(CN)_2]_2^{1-}$,

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TABLE I
Elemental analysis for $M(S_2C_2(CN)_2)_2^-$

$M(mnt)_2(Cation)_x$			C		H		N		
M	Cation	x	Calc	Obs	Calc	Obs	Calc	Obs	Melting point °C
Pt	$C_9H_8N^{+a}$	2	42.44	41.40	2.19	2.08	11.42	11.14	260–270°
Pt	$C_9H_8N^{+a}$	1	33.72	34.32	1.33	1.34	11.56	11.33	285–287°
Ni	NMP^+	1	47.21	47.44	2.08	2.08	15.73	15.48	>350°
Ni	NMP^+	2	55.98	56.06	3.04	3.14	15.36	15.19	200–210°
Ni	PPh_3He^+	1	52.61	52.53	2.94	3.00	9.09	8.87	198–200°
Ni	PPh_3Me^+	2	61.82	61.55	4.06	4.12	6.27	6.16	215–225°
Pt	PPh_3Me^+	1	43.08	43.09	2.41	2.50	7.44	7.45	198–200°
Pt	PPh_3Me^+	2	53.64	52.48	3.52	3.36	5.44	5.03	224–227°

[a] Quinolinium.

however detailed single crystal conductivity or crystallography has not been reported.[17]

Interrante and Browall[9] observed low conductivity for salts of the $M(S_2C_2H_2)_2^-$ (M=Ni,Pd,Pt) ion. Due to the greater electronegativity of the cyano group than the hydrogen atom as well as knowledge of the solid state structure of $(PPh_3Me)[Ni(S_2C_2(CN)_2)_2]$ we initiated an investigation of the electrical properties of $M(S_2C_2(CN)_2)_2^{1-}$(M=Ni,Pt).

EXPERIMENTAL

The triphenylmethylphosphonium, quinolinium, and *N*-methylphenazinium (NMP^+) salts were made according to a literature procedure[24] modified by the use of triphenylmethylphosphonium bromide, quinolinium chloride, and *N*-methylphenzinium methosulfate. Chemical analysis as received from Galbraith Laboratories are listed in Table I. A rotation photograph of $\underline{1}$ revealed the needle axis to be approximately 8.44 Å which agrees well with the *b*-axis of 8.41 Å for $Ph_3MePNi(mnt)_2$ as reported by Fritchie.[8] Comparison of powder x-ray results for $Ph_3MePPt(mnt)_2$ and $Ph_3MePNi(mnt)_2$ established the two systems as isomorphous.

Both two and four-probe single crystal conductivity measurements were made on several crystals of $(Ph_3)MeP^+[Pt(mnt)_2]^-$, $(Ph)_3MeP^+[Ni(mnt)_2]^-$, and $(NMP^+)[Ni(mnt)_2]^-$, and pressed pellets of $N(n\text{-}C_4H_9)_4^+[Ni(mnt)_2]^-$. The single crystal samples measured generally had dimensions of order 4 x 0.1 x 0.02 mm. Conductivities were measured for the direction parallel to the long axis which corresponds to the $Ni(mnt)_2^-$ stacking directly for the known $(Ph)_3MeP^+[Ni(mnt)_2]^-$ structure. The crystals were mounted on 0.001 inch diameter gold wires utilizing duPont No. 7941 silver paint. The measurements were carried out in a nitrogen atmosphere between 200°K and 400°K. The room temperature conductivity of all four systems was of order 10^{-10}(ohm-cm)$^{-1}$, but varied considerably between samples of the same material. This variation may have been due to variation in sample crystal quality (numbers of chain breaks and defects) as well as sample purity. Care was taken to ensure conductivities were being measured at voltages (electric fields) where the current was linear in voltage (in general, electric fields less than 100 volts/cm). For higher voltages nonlinearities were observed, i.e., $I \propto V^n$ with $n \gtrsim 2$.[2]

RESULTS AND DISCUSSION

The temperature dependence of the dc conductivity, σ_{dc}, was examined for $(Ph)_3MeP^+Pt(mnt)_2^-$, and $NMP^+Ni(mnt)_2^-$. Typical results are shown in Figure 1 for a $(Ph)_3MeP^+Pt(mnt)_2^-$ sample. The data for all these systems followed an Arrhenius expression, $\sigma \propto \exp(-E_a/k_BT)$, with activation energy E_a. The activation energies which are evaluated for $300°K < T < 400°K$ are given in Table II. They are large, i.e., ~ 0.5 eV, suggesting that there are few intrinsic carriers. For $T < 250°K$, a smaller E_a is frequently observed suggesting impurity dominated transport at these temperatures. A check of the frequency, f, dependence of conductivity for $265°K \leqslant T \leqslant 373°K$ for a $Ph_3MePNi(mnt)_2$ sample showed a frequency-independent conductivity for $f = \omega/2\pi < 100$ Hz,

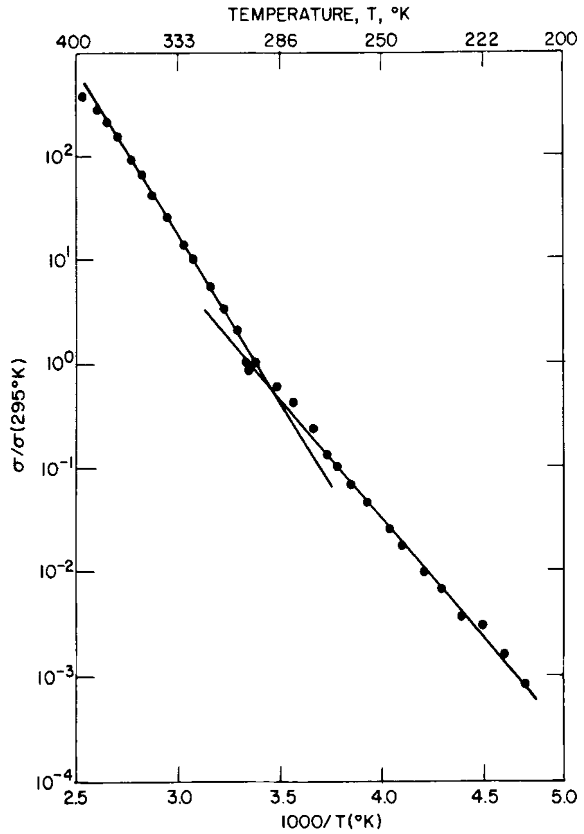
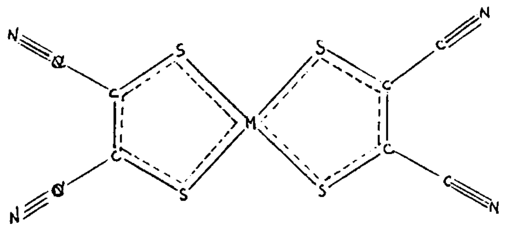


FIGURE 1 Temperature dependence of single crystal dc conductivity for $(Ph)_3MeP^+Ni(mnt)_2^-$ parallel to the stacking axis. The data is fit to ab Arrhenius expression, $\sigma \propto \exp(-E_a/k_BT)$, with $E_a = 0.55$ eV for $T > 285°K$ and $E_a = 0.42$ eV for $T < 285°K$.

TABLE II
Measured activation energies for $M(mnt)_2^-$

Complex	E_a, eV
$Ph_3MePNi(mnt)_2$	0.46 eV
$Ph_3MePPt(mnt)_2$	0.55 eV
$NMPNi(mnt)_2$	0.54 eV



with an increase in σ at higher frequencies (up to 10^5 Hz), approximately as $\omega^{1/2}$ with a constant prefactor A. That is, $\sigma = \sigma_{dc} + A\omega^{1/2}$, suggesting the dominance of hopping conduction at these frequencies.

The low conductivity must be understood in light of the known existence of one excess electron per site. Examining the molecular orbital levels of the metal bis-dithiolate system, it is seen that the highest occupied levels have a large "d" character to them,[25–27] however, the highest occupied molecular orbital is not the d_{z^2} orbital. For partially oxidised tetracyanoplatinate systems, the odd electron is in a molecular orbital of d_{z^2} character and hence overlaps with adjacent d_{z^2} MO's on adjacent sites to form an electron energy band. In contrast, for the mnt ligand field the d_{z^2} orbital is doubly occupied and the odd electron resides either in an orbital which has a small out-of-plane extension in space, i.e., d_{xz} and d_{yz}. Thus, the good overlap of the type observed for the tetracyanoplatinates is not achieved and the extremely low intrinsic conductivity indicates that this odd electron is unable to transfer to the neighbouring site because of poor orbital overlap. Hence this situation might be characterized as a Mott insulator.[28] Published magnetic resonance studies on the monomer in a matrix[25] confirm that the odd electron does not occupy the d_{z^2} orbital. In addition, susceptibility studies[29] have demonstrated single triplet behaviour implying spin interaction within dimers.

In sum, the bis-maleonitriledithiolate monoanion systems studied are poor conductors with magnetic interaction within dimers only. Because of the central role played by overlap between adjacent sites it appears that these systems offer an attractive vehicle for pressure dependent studies of transport properties in 1-D systems.

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