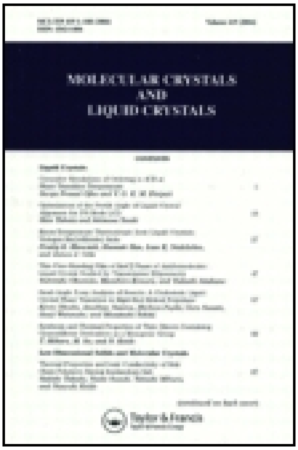

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Conducting Metal Dithiolate Complexes

A. E. Underhill [a] , M. M. Ahmad [a] , D. J. Turner [a] , P. I. Clemenson [a] , K. Carneiro [b] , Shen Yueqiuan [b] & K. Mortensen [c]

[a] Department of Chemistry and the Institute of Molecular and Biomolecular Electronics, University College of North Wales, Bangor, Gwynedd, Wales

[b] Physics Laboratory I, University of Copenhagen, Universitetsparken 5, DK 2100, Copenhagen, Denmark

[c] Physics Department, Risø National Laboratory, DK 4000, Roskilde, Denmark

To cite this article: A. E. Underhill , M. M. Ahmad , D. J. Turner , P. I. Clemenson , K. Carneiro , Shen Yueqiuan & K. Mortensen (1985): Conducting Metal Dithiolate Complexes, Molecular Crystals and Liquid Crystals, 120:1, 369-376

To link to this article: http://dx.doi.org/10.1080/00268948508075822

Mol. Cryst. Liq. Cryst. 1985, Vol. 120, pp. 369-376
0026-8941/85/1204-0369/$15.00/0

CONDUCTING METAL DITHIOLATE COMPLEXES

A.E. UNDERHILL, M.M. AHMAD, D.J. TURNER, P.I. CLEMENSON
Department of Chemistry and the Institute of Molecular
and Biomolecular Electronics, University College of North
Wales, Bangor, Gwynedd, Wales,
K. CARNEIRO, SHEN YUEQIUAN,
Physics Laboratory I, University of Copenhagen,
Universitetsparken 5, DK 2100 Copenhagen, Denmark,
K. MORTENSEN,
Physics Department, Risϕ National Laboratory, DK 4000
Roskilde, Denmark.

Abstract Further work on the chemical composition of the one-dimensional metallic metal dithiolene complex Li-Pt(mnt) is reported. The electrical conduction and thermopower properties of the nickel and palladium complexes are reported and compared with those of the platinum compound.

Within the field of synthetic metals and superconductors there is a constant search for new materials that display novel properties or whose properties can be used to test theoretical models of these sytems. The discovery, a few years ago, of a new type of one-dimensional metal, the lithium salt of $[Pt(mnt)_2]^{n-}$, Li-Pt(mnt), (where mnt = Z dicyanobut-2-ene dithiolate, $C_4N_2S_2{}^{2-}$) has prompted extensive work on this class of compound.[1-5] Following initial reports of the preparation,[1] electrical conduction[2] and crystal structure at room temperature[3] a detailed study of the physical properties[4] and the Peierls structure[5] of this compound have been made. We now report further work on this class of compound.

CHEMICAL COMPOSITION OF Li-Pt(mnt)

The 1-D conductor Li-Pt(mnt) is prepared by the following route.

A solution of $(Et_4N)_2[Pt(mnt)_2]$, in 70% acetone/water is passed down a protonated ion exchange resin column (Dowex 20W-50) and an excess of LiCl is added to the eluted solution. Slow aerial oxidation and evaporation of the solution over several weeks yields a black solid. This solid consists of small needle shaped crystals of Li-Pt(mnt) and small black platelets. The small black platelets have been shown to be $Li_{0.5}[Pt(mnt)_2]\cdot 2H_2O$ (β-Li-Pt(mnt)).[6]

Initial analysis of Li-Pt(mnt) showed that the lithium content was about 1% and this together with analysis for Pt, C, N and H suggested an empirical formula of $Li_{0.8}[Pt(mnt)_2]2H_2O$.[2] Structural studies supported this by showing partial occupation of the Li^+ sites and indicating a Peierls distortion at low temperatures with $2k_F = 0.82$ or 1.18.[5]

Recent studies, however, indicated a positive value of the thermopower above T_C suggesting a greater than half-filled band.[4] This would be in agreement with $2k_F = 1.18$ and suggested an average charge of -1.18 on the $[Pt(mnt)_2]$ anions. This clearly requires the presence of other cations in addition to the lithium ions found by chemical analysis. Previous studies on partially oxidised tetracyanoplatinate salts grown from acidic solutions have shown that H_3O^+ ions can be incorporated in the lattice in addition to, or in place of, monovalent metal cations.[7] Further chemical investigation of Li-Pt(mnt) was therefore undertaken.

Determination of the charge on the $[Pt(mnt)_2]$ anion

Iodine is known to oxidise the di-anion $[Pt(mnt)]^{2-}$ to the mono anion, $[Pt(mnt)_2]^-$. A weighed sample of Li-Pt(mnt) was dissolved in water and a known amount of aqueous I_2 added. The excess I_2 was back titrated with standard $Na_2S_2O_3$ using modified starch as an indicator. The average negative charge on the $[Pt(mnt)_2]^{n-}$ anion in solution of three separate samples was found to be 1.15, 1.15 and 1.18. These are close to the value of 1.18 expected from the structural studies and support the thermopower results in indicating a greater than half-filled band. The discrepancy between the values derived from chemical analysis and from X-ray experiments is greater than experimental error and may arise from sampling problems. The preparation yields two compounds which have to be separated by hand and slight contamination of Li-Pt(mnt) by $Li_{0.5}Pt(mnt)_2 \cdot 2H_2O$, possibly in the form of small particles on the surface of the needles, would have the effect of reducing the value of the charge calculated for the anion.

Determination of the H_3O^+ content

The H_3O^+ content of the Li-Pt(mnt) crystals was determined by dissolving a weighed sample in water and titrating the H_3O^+ liberated with 5×10^{-4} M NaOH using a Pt electrode to detect the end-point. Results from two separate preparations of Li-Pt(mnt) both showed $0.33H_3O^+$ ion per $[Pt(mnt)_2]$ anion. The original Li, C, H, N and Pt analyses, the charge determined for the cation, the H_3O^+ content and the X-ray value of 2 k_F of 1.18 now present a consistent picture for the composition of Li-Pt(mnt) and this compound should now be represented by the empirical formula

$$Li_{0.8}(H_3O)_{0.33}[Pt(S_2C_4N_2)_2] \cdot 1.67H_2O.$$

COMPARISON OF THE PROPERTIES OF $Li_x[M(mnt)_2] \cdot 2H_2O$ (where M = Ni, Pd or Pt)

As described earlier slow aerial oxidation and evaporation of an acetone/water solution of $H_2[Pt(mnt)_2]$ in the presence of LiCl gave a mixture of needle shaped crystals of Li-Pt(mnt) and plate shaped crystals of $Li_{0.5}[Pt(mnt)_2] \cdot 2H_2O$. Under similar conditions $H_2[Ni(mnt)_2]$ gave on one occasion black needle shaped crystals but more generally a black microcrystalline powder. Under these conditions the corresponding palladium compound is not oxidised because of the differences in the $[M(mnt)_2]^{2-} \rightarrow [M(mnt)_2]^-$ redox potentials for the Pt, Pd and Ni salts. However, a black microcrystalline product is obtained by electrocrystallisation of a solution of $H_2[Pd(mnt)_2]$ in the presence of LiCl or $LiClO_4$.

$Li_x[Ni(mnt)_2]\cdot 2H_2O$ (Li-Ni(mnt))

Preliminary X-ray studies[8] have shown that the unit cell dimensions of Li-Ni(mnt) (orthorhombic, a = 31.82; b = 11.65; c = 3.74 A) are different from those of Li-Pt(mnt)[3] (triclinic, P1, a = 15.596(4); b = 6.410(3); c = 3.639(2) A; α = 100.52(9); β = 90.75(5); γ = 96.28(6)°) but unfortunately the crystal quality was too poor for a complete structure determination.

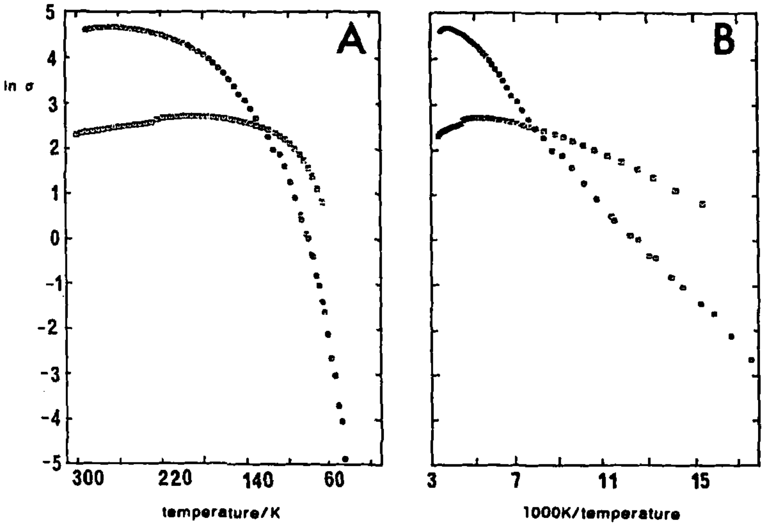

FIGURE 1 Variation of electrical conductivity of Li-Pt(mnt) (o o o) and Li-Ni(mnt) (□ □ □) with temperature (A) and with inverse temperature (B).

The room temperature conductivity of the crystals along the needle axis, σ_{RT} = 10 S cm^{-1}, is an order of magnitude lower than that found for the platinum compound. Figure 1, shows that the variation of conductivity with temperature for the two compounds is significantly different in two respects. The transition temperature for the metal to semiconductor transition clearly occurs at a much lower temperature in the nickel compound, and the transition is smeared over a wider temperature range. From the data it also appears that the activation energy for conduction in the semiconducting region may be less than that of the platinum salt but more data at lower temperatures are needed to confirm this. A smaller value for the band gap and a reduced value of T_c compared with the platinum compound would suggest a more one-dimensional compound and account for the smearing of the transition by fluctuations.

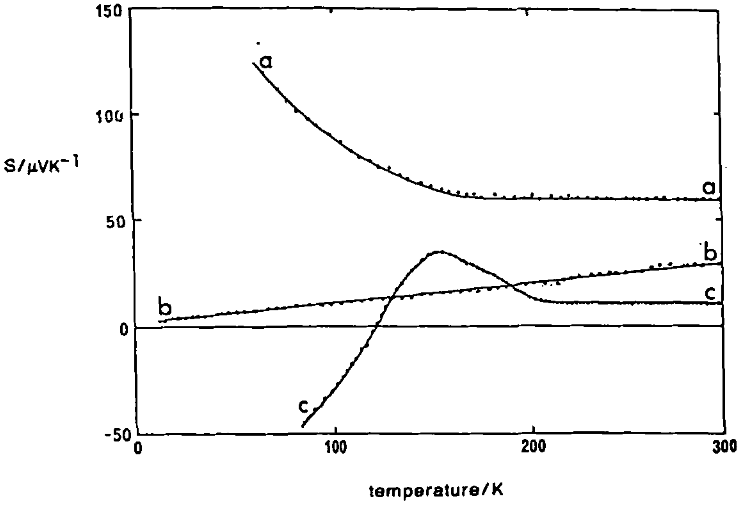

FIGURE 2 Variation of thermopower with temperature for Li-Ni(mnt) (single crystal, a), Li-Pd(mnt) (pellet, b) and Li-Pt(mnt) (single crystal, c).

The variation of thermopower with temperature is shown in Figure 2. The thermopower is positive at room temperature (+ 60 μVK^{-1}) and is almost independent of temperature down to 190 K. In this respect it is very similar to the behaviour of Li-Pt(mnt) except that the value is more positive and hence, assuming the band filling is the same, indicating a narrower electronic band width. In fact the value of the thermopower is close to that value expected, $(k_B/e)\ln 2 = 60\ \mu VK^{-1}$, when the spin-entropy dominates the thermopower. This arises when strong on-site Coulomb repulsion causes separation of spin- and charge degrees of freedom and the charge contribution to the thermopower vanish. E.g. this is the case observed for quarter-filled narrow band TCNQ conductors.[9] This may indicate that Coulomb correlation effects are important in the nickel compound whereas earlier studies showed them not to be significant in the platinum compound.[4] At lower temperatures the thermopower shows a very smeared transition in agreement with the conductivity results. From room temperature to 70 K the thermopower becomes increasingly positive and there is no sign of the reversal of slope observed in the platinum compound and assigned to donor defect states in the gap.[4]

$Li_x[Pd(mnt)_2]\cdot 2H_2O$ (Li-Pd(mnt))

The palladium salt has been obtained only as a microcrystalline powder and physical measurements have therefore been made on compressed pellets.

The conductivity of a pellet of Li-Pd(mnt) at room temperature ($\approx 1\ S\ cm^{-1}$) is comparable to those obtained on pellets of Li-Pt(mnt). Pellets of the palladium compound also show evidence of a metal to semiconductor transition with the suggestion of a lower transition temperature and a lower activation energy than observed for Li-Pt(mnt). The thermopower (see Figure 2), however, shows a more dramatic difference between the two compounds. The palladium compound exhibits a small positive thermopower ($+ 29\ \mu VK^{-1}$) at room temperature which decreases slowly to $+2\ \mu VK^{-1}$ at 10 K. There is no sign of a metal to insulator transition and hence the thermopower suggests metallic behaviour down to very low temperatures. The striking difference in the characteristics of the conductivity and of the

thermopower of the Pd compound may be attributed to grain boundary effects which will be resistive for conductivity measurements but will not affect the thermopower because zero current flows in this measurement. Similar results have been observed for other one-dimensional conductors.[10]

GENERAL DISCUSSION

Recent extended Huckel MO calculations on Li-Pt(mnt) have confirmed that intrastack overlap is predominantly associated with the ligands and particularly the sulphur orbitals.[5] However the central metal d_{xz} and d_{yz} orbitals play an important role in delocalising charge across the whole anion. Little has shown that, because of the relative energies of the atomic orbitals, Pd-S overlap will be stronger than either Ni-S or Pt-S.[11] The results described here may be understood in terms of this model. In Li-Ni(mnt) the lower energy of the $3d_{xz}$ and $3d_{yz}$ orbitals will result in less delocalisation of charge throughout the complex anion and hence greater correlation effects as suggested by the thermopower results. In Li-Pd(mnt) delocalisation may be maximised and the metallic state appears to be preserved down to low temperatures.

We would like to thank the SERC for support and Johnson Matthey & Co Ltd for the loan of precious metal salts.

REFERENCES

1. **A.E. Underhill and M.M. Ahmad, J. Chem. Soc. Chem. Commun., 67, (1981).**
2. **M.M. Ahmad and A.E. Underhill, J. Chem. Soc., 1065 (1982).**
3. **A. Kobayashi, T. Mori, Y. Sasaki, H. Kobayashi, A.E. Underhill, and M.M. Ahmad, J. Chem. Soc. Chem. Commun., 390 (1982).**
4. **M.M. Ahmad, D.J. Turner, A.E. Underhill, C.S. Jacobsen, K. Mortensen and K. Carneiro, Phys. Rev. (B), 29, 4796 (1984).**
5. **A. Kobayashi, T. Mori, Y. Sasaki, H. Kobayashi, M.M. Ahmad and A.E. Underhill, Bull. Chem. Soc. Jpn, submitted for publication.**

6. A. Kobayashi, Y. Sasaki, H. Kobayashi, A.E. Underhill and M.M. Ahmad, Chem. Lett., 305 (1984).
7. D.J. Wood and A.E.Underhill, J. Chem. Soc., Dalton Trans., 360 (1980).
8. A. Kobayashi and H. Kobayashi, private communication.
9. P.M. Chaikin and G. Beni, Phys. Rev. (B), **13**, 647 (1976).
10. Y.W. Park, A. Denenstein, G.K. Chiang, A.J. Heeger and A.G. MacDiarmid, Solid State Commun., **29**, 747 (1979).
11. W.A. Little, J. du Physique, **44**, C3-819 (1983).