A Study of the One-dimensional Conductor $Li_{0.75}[Pt\{S_2C_2(CN)_2\}_2]\cdot 2H_2O$

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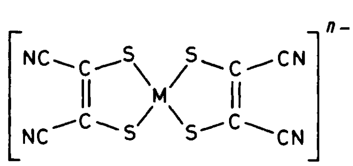
The preparation, and a detailed study of electrical conduction properties, of $Li_{0.75}[Pt(S_2C_4N_2)_2]\cdot 2H_2O$ are described. The electrical conduction properties are compared with those of other one-dimensional metals.

CONSIDERABLE interest has been shown over the past decade in inorganic and organic compounds whose solid-state properties exhibit highly anisotropic optical, transport, or co-operative magnetic phenomena.[1-4] Extensive work has been carried out to synthesise and study a large range of inorganic one-dimensional metals based on the square coplanar tetracyanoplatinate and bis(oxalato)platinate anions.[1,4] These studies have provided a valuable insight into the relationship between chemical composition, structure, and solid-state properties in this class of compounds.

Two criteria appear necessary for square coplanar tetracyanoplatinate and bis(oxalato)platinate complexes to exhibit high and anisotropic electrical conduction properties. First, the square coplanar complexes must form a columnar stack structure with a short intrachain metal–metal separation. Secondly, the metal atom or complex as a whole must adopt a non-integral formal oxidation state. In both series of compounds the transport properties can be explained completely in terms of the charge carrier being confined to the metal-atom chain. The co-ordinating ligands do not participate directly in the conduction mechanism. Studies on a series of partially oxidised tetracyanoplatinate salts have shown the crucial relationships between structure and intrachain separation, degree of partial oxidation, and electrical conductivity.[5]

It is of prime importance to the understanding and possible technological application of the solid-state properties of highly anisotropic conductors that the range of materials for study should be extended. For the last decade or more a group of compounds has been known, based on transition-metal complexes of 1,2-dicyanoethylene-1,2-dithiolate (maleonitriledithiolate, mnt), and possessing widely different electrical conduction properties.[6-8] This ligand can stabilise transition metals in a variety of oxidation states and the high electron affinity of the terminal cyanide groups aids the delocalisation of charge within the complex, thus reducing potential coulombic repulsions. Both mono- and di-anion complexes are formed with bivalent transition-metal ions and these are found to stack face-to-face in the crystal lattice.[9,10] Thus it might be expected that complexes of this ligand with suitable metals might be developed as highly anisotropic conductors. Most of the studies made previously on compounds containing $[M(mnt)_2]^{n-}$ anions (where M = Ni, Pd, or Pt) were carried out on the salts of bulky cations.[7,8] These compounds have been shown to be poor conductors or insulators but work with the tetracyanoplatinates[5] indicates that the size of the cation may play a vital role in allowing a short intrachain metal–metal separation. The one exception, '$(perylene)_2[Pt(mnt)_2]$', exhibits metallic properties due to conduction through the organic cations.[11] The observation of relatively high room-temperature conductivity for compressed discs of $Na[M(mnt)_2]\cdot 1.5H_2O$ (where M = Ni or Pd) also indicated that this class of compound was worthy of further study.[12] We have therefore investigated a series of compounds of Ni and Pt with this ligand and containing a range of small cations. We report here our studies on the new one-dimensional metal $Li_{0.75}[Pt(mnt)_2]\cdot 2H_2O$. A preliminary account of this work has been reported elsewhere.[13]



EXPERIMENTAL

Preparation of $Li_{0.75}[Pt(mnt)_2]\cdot 2H_2O$.—Sodium 1,2-dicyanoethylene-1,2-dithiolate was prepared and recrystallised from $EtOH-Et_2O$.[14] $K_2[PtCl_4]$ (4.16 g, 0.01 mol) was dissolved in water (30 cm^3) and a H_2O–EtOH (50 : 50, 60 cm^3) solution of $Na_2(mnt)$ (4.4 g, 0.023 mol) added. Addition of NEt_4Br (5 g, 0.023 mol) in EtOH (25 cm^3) gave a precipitate of $[NEt_4]_2[Pt(mnt)_2]$.[15] A solution of $[NEt_4]_2[Pt(mnt)_2]$ (3 mmol dm^{-3}) in acetone–water (70 : 30) was passed through an ion-exchange column containing Dowex 50W X8 in the acid form. The resulting solution of $H_2[Pt(mnt)_2]$ was mixed with an aqueous solution of the mol equivalent amount of LiCl. Slow aerial oxidation and evaporation of this solution gave, over 10 weeks, shiny black crystals of the product (typical size 2.6 × 0.13 × 0.10 mm) which were filtered off, washed with water, and air dried (Found: C, 18.2; H, 0.55; Li, 0.95; N, 11.35; Pt, 36.5; H_2O, 7.0. Calc. for $C_8H_4Li_{0.75}N_4O_2PtS_4$: C, 18.6; H, 0.75; Li, 1.00; N, 10.85; Pt, 37.8; H_2O, 6.95%). The quality or size of the crystals obtained was not improved by the addition of either oxalic acid or urea to the solution.

Analysis.—Lithium and platinum analyses were carried out by Dr. E. Pascher, Microanalytical Laboratory, Bonn, Germany. Lithium was also determined independently by atomic emission. Carbon, hydrogen, and nitrogen were determined microanalytically. The water content was determined by thermogravimetric analysis (t.g.a.) and corresponds to the weight loss in the temperature range 50—133 °C.

Physical Measurements.—Solution spectra were recorded using a Beckman DK-2A spectrophotometer, and e.s.r. on a Varian e.s.r. spectrometer at *X*- and *Q*-band frequencies and 100 kHz modulation.

Single-crystal *X*-ray diffraction measurements were carried out using a Stoe Weissenberg camera and Cu-K_α radiation.

Electrical conduction measurements were carried out as previously described.[16] Aquadag (colloidal graphite in water) was used as the contact material between the crystal and the 0.001 in diameter gold wires. All crystals gave ohmic behaviour under the conditions of measurement.

RESULTS AND DISCUSSION

Electrical Conduction.—The complex $Li_{0.75}[Pt(mnt)_2]\cdot 2H_2O$ forms thin needle-shaped crystals and the electrical conduction properties could only be measured along the needle axis. Crystals from three different preparations were studied and consistent properties were observed for freshly cropped crystals and for crystals stored at a relative humidity of 76%. The conductivity along the needle axis at room temperature (r.t.) determined by the four-probe d.c. technique for 43 crystals lay in the range 30—212 Ω^{-1} cm^{-1}. The highest values were observed for freshly cropped crystals dried at r.t. under ambient humidity for 2 h prior to measurement. Crystals stored for a period of weeks under ambient humidity exhibited the lower values probably due to changes in the hydration of the crystals (see studies on dehydrated crystals). These crystals are susceptible to changes in hydration partly due to the large surface area to volume ratio. Similar effects have been observed in other highly conducting hydrated crystals.[17] Charge-exhaustion experiments established that the conduction mechanism was not either ionic or protonic in nature.

For $Li_{0.75}[Pt(mnt)_2]\cdot 2H_2O$ the maximum values observed for $\sigma_{\parallel}$ of *ca.* 212 Ω^{-1} cm^{-1} are comparable with the conductivity along the stacking axis of other highly conducting metal complexes such as $K_2[Pt(CN)_4]Br_{0.3}\cdot 3H_2O$ (*ca.* 300 Ω^{-1} cm^{-1})[18] and '(perylene)$_2$[Pt(mnt)$_2$]' (*ca.* 280 Ω^{-1} cm^{-1}).[11]

The temperature dependence of $\sigma_{\parallel}$ over the range 292—30 K was determined on 16 crystals of $Li_{0.75}[Pt(mnt)_2]\cdot 2H_2O$. The variation of $\sigma_{\parallel}$ with temperature between 180 and 292 K is shown in Figure 1 for three representative crystals. The conductivity of freshly cropped crystals slowly increases with decreasing temperature, with $\sigma_{\parallel}$ passing through a maximum around 250 K. The conductivity falls to the r.t. value at *ca.* 200 K and thereafter falls rapidly with decreasing temperature. This metallic-like behaviour around r.t. is very similar to that observed for $K_2[Pt(CN)_4]Br_{0.3}\cdot 3H_2O$[18] and other one-dimensional metallic complexes of platinum.[5] All the fresh crystals studied exhibited this behaviour. Crystals stored at a relative humidity of 75% show a maximum at *ca.* 260 K and a sharp fall in conductivity below 200 K but, however, the maximum was less pronounced than for the freshly cropped crystals. Crystals stored for weeks under ambient humidity did not show any conductivity maximum with decreasing temperature but instead showed a temperature-independent region down to 240 K, followed by a slow fall to *ca.* 180 K, and thereafter a rapid fall in conductivity below this temperature. The above variation would appear to be connected with changes in the degree of hydration of the crystals. Similar effects have also been observed for other hydrated one-dimensional metallic conductors.[17] It was observed that the quality of the crystal also affected the temperature dependence of the conductivity; only high quality crystals displayed a conductivity maximum.

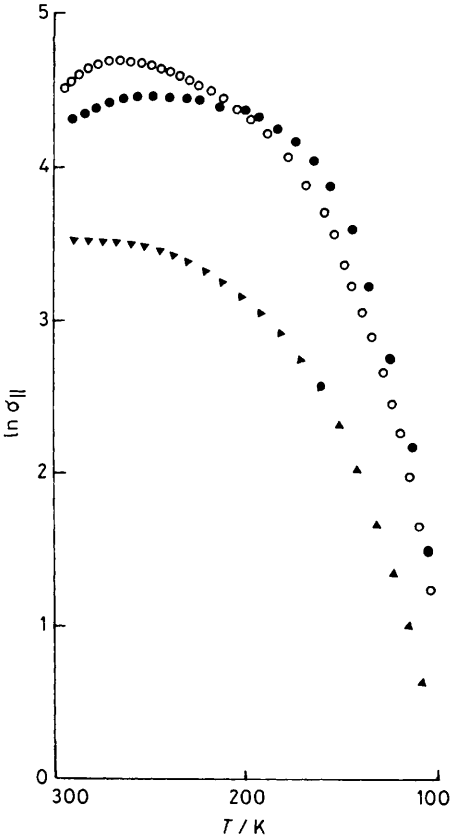


FIGURE 1 Variation of conductivity with temperature for crystals of $Li_{0.75}[Pt(mnt)_2]\cdot 2H_2O$: (○) freshly cropped; (●) crystals stored at 75% relative humidity; (▼) stored at ambient humidity for 14 d

Figure 2 shows the variation of $\sigma_{\parallel}$, normalised relative to the r.t. conductivity, *versus* inverse temperature over the whole temperature range studied. It can be seen that the temperature dependence of the conductivity of the compound over the complete range is very similar to that of $K_2[Pt(CN)_4]Br_{0.3}\cdot 3H_2O$ and related compounds.[5,17] Below 100 K there is an approximately linear dependence of ln $\sigma_{\parallel}$ with inverse temperature corresponding to an activation energy of *ca.* 34 meV.*

The results discussed above suggest that the electrical conduction properties are very dependent on the degree of hydration of the crystals. To investigate this further two crystals were studied before and after being placed

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* Throughout this paper: 1 eV ≈ 1.60 × 10^{-19} J.

under dehydrating conditions. For one crystal the r.t. conductivity fell from 64 to 3 Ω^{-1} cm^{-1} after being stored over silica gel for 3 d whilst that of another fell from 72 to 0.7 Ω^{-1} cm^{-1} after being dried at 373 K for 4 h. The variation of conductivity with inverse temperature of these two crystals is shown in Figure 3. For both crystals the conductivity decreased with decreasing temperature (from r.t.) and there was no evidence of a temperature-independent region. The activation energy for conduction appears to increase with increasing dehydration being *ca.* 48 for the crystal stored over silica gel and *ca.* 59 meV for the crystal heated under vacuum.

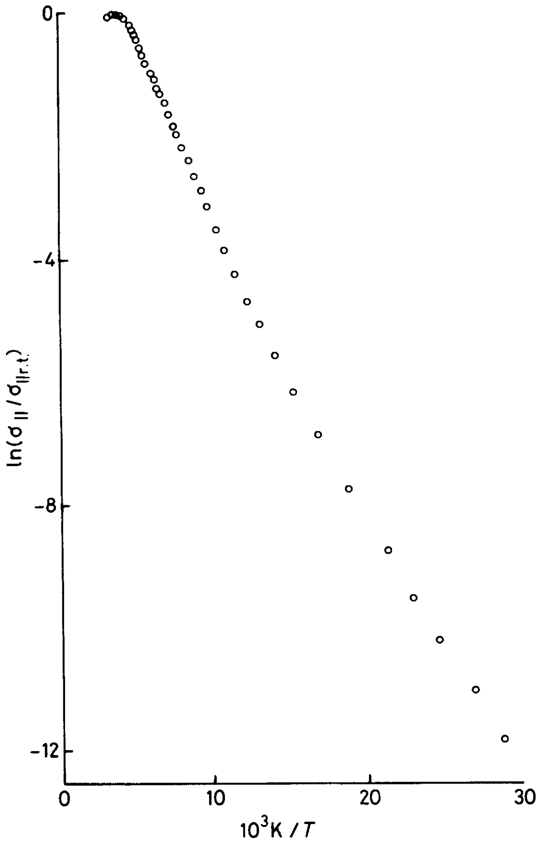

FIGURE 2 Variation of conductivity, $\ln(\sigma_{\parallel}/\sigma_{\parallel r.t.})$, with inverse temperature for $Li_{0.75}[Pt(mnt)_2]\cdot 2H_2O$

Optical Studies.—The preparation of $Li_{0.75}[Pt(mnt)_2]\cdot 2H_2O$ involves the slow aerial oxidation and evaporation of an aqueous–acetone solution of $H_2[Pt(mnt)_2]$ and LiCl. During this process the solution changes from red to brown-black and eventually black crystals of the complex are deposited. Figure 4 illustrates the difference in the absorption spectrum of a solution of a simple dianion salt $[NEt_4]_2[Pt(mnt)_2]$ with that of the solution obtained from the cation-exchange resin containing $H_2[Pt(mnt)_2]$ measured immediately after preparation. It can be seen that the spectrum of the acid is much more intense than that of the salt and contains additional bands. This spectrum suggests that oligomers of the dianion species are produced at low pH. Figure 4 also shows the spectrum of a dilute solution of $Li_{0.75}[Pt(mnt)_2]\cdot 2H_2O$ which exhibits an intense absorption band at 4 950 cm^{-1} and a weak band at 11 764 cm^{-1}.

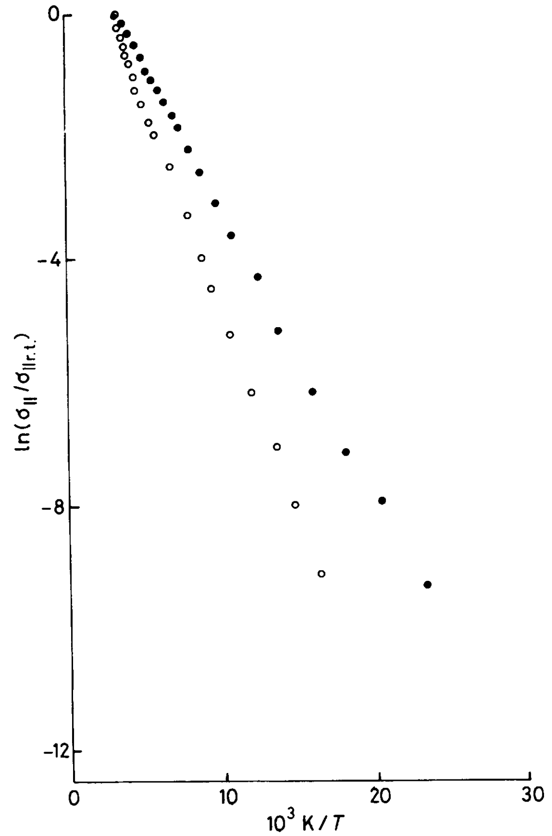

FIGURE 3 Variation of conductivity, $\ln(\sigma_{\parallel}/\sigma_{\parallel r.t.})$, with inverse temperature for dehydrated crystals of $Li_{0.75}[Pt(mnt)_2]\cdot 2H_2O$: (●) stored over silica gel (3 d); (○) heated at 373 K (4 h)

Single crystals of one-dimensional metallic complexes such as $K_2[Pt(CN)_4]Br_{0.3}\cdot 3H_2O$ are strongly dichromic in polarised light [19] but crystals of $Li_{0.75}[Pt(mnt)_2]\cdot 2H_2O$ appear uniformly black under these conditions. Reflectivity studies with light polarised parallel to the needle axis of the crystal indicate a plasma frequency at *ca.* 6 000 cm^{-1}.[20] This is in the region observed for organic

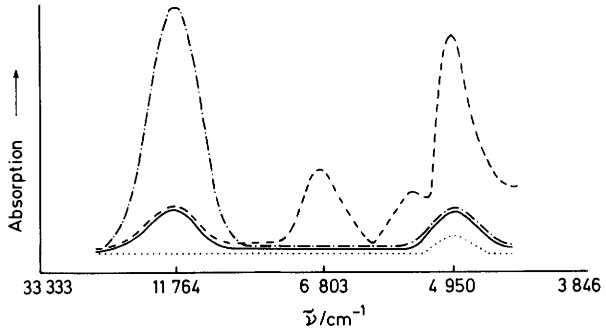

FIGURE 4 Absorption spectra of $[Pt(mnt)_2]^{2-}$ salts in acetone–water (60 : 40): (– – – –) $H_2[Pt(mnt)_2]$ (2.7 × 10^{-5} mol dm^{-3}); (— · — · —) $Li_{0.75}[Pt(mnt)_2]\cdot 2H_2O$ (3 × 10^{-4} mol dm^{-3}); (——) $[NEt_4]_2[Pt(mnt)_2]$ (4.6 × 10^{-3} mol dm^{-3}); (· · · ·) solvent

one-dimensional metals and is considerably lower than that found for the one-dimensional metallic complexes such as $K_2[Pt(CN)_4]Br_{0.3}\cdot3H_2O$ [21] and $Zn_{0.87}[Pt(C_2O_4)_2]\cdot6H_2O$.[22]

X-P.E.S. Studies.—Previous studies on $[NEt_4][Pt(mnt)_2]$ and $[NEt_4]_2[Pt(mnt)_2]$ showed the Pt $4f_{\frac{7}{2}}$ and Pt $4f_{\frac{5}{2}}$ binding energies to be very similar in spite of the presence of an extra electron on the dianion species.[23] This similarity was attributed to the additional electron being mainly localised on the cyano-groups of the ligand rather than on the platinum atom.[23] The results shown in the Table confirm this observation. The *X*-p.e.s. spectrum of $Li_{0.75}[Pt(mnt)_2]\cdot2H_2O$ also contains only two peaks corresponding to the Pt $4f_{\frac{7}{2}}$ and $4f_{\frac{5}{2}}$ binding energies. These are significantly higher than those observed in the mono- and di-anion salts presumably due to the strong intermolecular bonding between adjacent $[Pt(mnt)_2]^{n-}$ anions in $Li_{0.75}[Pt(mnt)_2]\cdot2H_2O$ and which is absent in the simple NEt_4^+ salts.

Binding energies (eV) for platinum complexes *

Complex	Pt $4f_{\frac{7}{2}}$	Pt $4f_{\frac{5}{2}}$
$Li_{0.75}[Pt(mnt)_2]\cdot2H_2O$	74.0	77.0
$[NEt_4]_2[Pt(mnt)_2]$	73.0	76.3
$[NEt_4][Pt(mnt)_2]$	72.9	76.3

* Binding energies are relative to that of the carbon 1*s* electron from the ethyl groups in the compounds, which was taken as 285.0 eV; the uncertainty in the measured binding energy is *ca.* ±0.3 eV.

General Discussion.—The stoicheiometry of $Li_{0.75}[Pt(mnt)_2]\cdot2H_2O$ suggests that this is the first reported partially oxidised $[Pt(mnt)_2]^{n-}$ analogue of the cation-deficient tetracyanoplatinate and bis(oxalato)platinate salts. Unfortunately it has not been possible to confirm the non-integral oxidation state of the anion by either direct chemical means or by the presence of diffuse *X*-ray scattering. However, the high r.t. conductivity and the temperature dependence of the conductivity supports this assertion. The temperature dependence illustrated in Figure 2 is very similar to that previously reported for $K_2[Pt(CN)_4]Br_{0.3}\cdot3H_2O$ [17] and [Ni(pc)]I [24] (pc = phthalocyaninate).

The conduction mechanisms proposed for these latter compounds are quite different. In $K_2[Pt(CN)_4]Br_{0.3}\cdot3H_2O$ the conduction pathway is based on a partially filled band produced by overlap of the platinum $5d_{z^2}$ orbitals, the short intrachain platinum-atom separation in $K_2[Pt(CN)_4]Br_{0.3}\cdot3H_2O$ (2.89 Å) being only slightly longer than that observed in Pt metal itself (2.78 Å). In [Ni(pc)]I the conduction pathway is associated with whole Ni(pc) molecules which are stacked above one another with an intra-planar separation of 3.244 Å. For a nickel complex this distance is too large to form a conduction pathway based on the overlap of the $3d_{z^2}$ orbitals. The e.s.r. spectrum of [Ni(pc)]I shows radical-ion signals in contrast to the absence of an e.s.r. signal in $K_2[Pt(CN)_4]Br_{0.3}\cdot3H_2O$. This indicates that the whole Ni(pc) molecule is taking part in the conduction mechanism which is probably similar to that found in the conducting tcnq and ttf compounds (tetracyanoquinodimethane and tetrathiofulvalene respectively).

Preliminary *X*-ray studies on $Li_{0.75}[Pt(mnt)_2]\cdot2H_2O$ indicate that the repeat distance along the conducting axis of the crystal is 3.60 Å. This is presumably the Pt–Pt separation and suggests that the extent of $5d_{z^2}$ orbital overlap between adjacent platinum atoms in the chain will be small. No radical-ion signal was observed in e.s.r. measurements down to 78 K. Thus the properties of $Li_{0.75}[Pt(mnt)_2]\cdot2H_2O$ do not readily place it in a class of one-dimensional conductors similar to $K_2[Pt(CN)_4]Br_{0.3}\cdot3H_2O$ or [Ni(pc)]I.

Further work is in progress to elucidate the structure and properties of the compound and to extend the range of compounds by changing the cation, the central metal, and the substituents in the ligand.

We thank Mr. S. J. Beam (Johnson Matthey Research Centre) for the *X*-p.e.s. spectra, the S.R.C. for support, and Johnson Matthey & Co. Ltd. for the loan of platinum salts. One of us (A. E. U.) wishes to acknowledge the support of N.A.T.O. (Grant no. 016.81).

[1/1735 *Received, 9th November,* 1981]

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