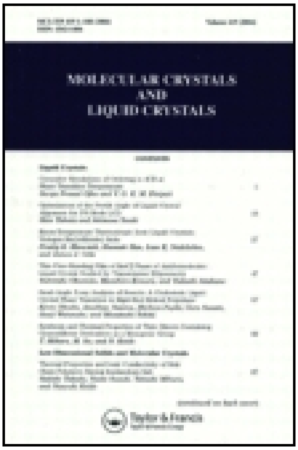

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New 1-D Metals Based on BIS(DICYANOETHYLENEDITHIOLATO Platinum Salts of Small Cations

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NEW 1-D METALS BASED ON BIS(DICYANOETHYLENEDITHIOLATO)-PLATINUM SALTS OF SMALL CATIONS*

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The preparation and properties of a series of compounds of formulae $M_{0.75}[Pt(S_2C_4N_2)_2]\cdot xH_2O$ (where M is Li^+ or NH_4^+) or $Mg_{0.4}[Pt(S_2C_4N_2)_2]\cdot yH_2O$ are described. Studies of the reflectance spectra of powdered samples and electrical conduction measurements on compressed pellets of these compounds indicates that the extent of the interaction between the $[Pt(S_2C_4N_2)_2]^{n-}$ anions falls in the order $Li^+ > Mg^{2+} > NH_4^+$. Single crystals of $Li_{0.75}[Pt(S_2C_4N_2)_2]\cdot 1.5H_2O$ exhibit metallic conduction properties around room temperature with a maximum value of about 200 Ω^{-1} cm^{-1} at 250 K. The temperature dependence of the conductivity is similar to that of the partially oxidised platinum atom chain compounds.

It is very important to the understanding and the possible application of one-dimensional metals that the range of materials available for detailed study should be extended. Within the class of 1-D metals based on partially oxidised chains of metal atoms most of the work has concentrated on the tetracyanoplatinate, bis(oxalato)platinate, and iridium carbonyl halide salts.[1] A group of compounds based on anionic transition metal complexes of 1,2-dicyanoethylene-1,2-dithiol (mnt) have been known to possess a wide range of conduction properties for many years.[1-5] However, until

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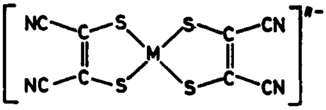
very recently, none of these compounds had been shown to possess metallic properties based on conduction through the anionic metal complex.[6] Previously 1-D metals containing these complex anions had only been prepared in which conduction occurs through the organic cation.[7]



Square coplanar complexes of mnt possess many of the properties required for the formation of a 1-D metal. The anions can occur in a variety of oxidation states and the terminal cyanide groups can aid the delocalisation of charge within the complex thus reducing potential coulombic repulsion. Both uni- and di-anion complexes are formed with divalent transition metal ions and these are often found to form stacks in the crystal lattice.[8] However, direct overlap of metal orbitals on adjacent anions has not been observed and all examples to date have a staggered arrangement of anions. Dimer formation is also common.[2,8]

Most of the previous studies have been made on the salts of bulky cations which might be expected to prevent the close approach of anions in the lattice. The work described here is concerned with the salts of the $[Pt(S_2C_4N_2)]^{n-}$ anion with small cations, which it was considered would maximise the likelihood of 1-D metallic properties. This work was, in part, stimulated by the observation of high conductivity for compressed discs of $Na[M(S_2C_4N_2)_2]\cdot 1.5H_2O$ (where M = Ni or Pd).[5] A preliminary account of the work on $Li_{0.75}[Pt(S_2C_4N_2)_2]\cdot 1.5H_2O$ has been reported.[6]

EXPERIMENTAL

The compounds were prepared by passing an acetone/water solution of $(Et_4N)_2[Pt(S_2C_4N_2)_2]$ through an ion exchange column containing Dowex 50W X8 in acid form. The resulting solution of $H_2[Pt(S_2C_4N_2)_2]$ was mixed with an aqueous solution containing the mole equivalent of LiCl, $MgCl_2$, or NH_4Cl. Slow aerial oxidation and evaporation of this solution over a period of 10 weeks deposited the products. The lithium salt was obtained as black shiny needle-shaped crystals (typical size 2.6 x 0.13 x 0.10 mm) whereas the magnesium and ammonium compounds were obtained as microcrystalline precipitates.

RESULTS AND DISCUSSION

Elemental analysis of the products indicates that the compounds do not have a simple cation to anion stoichiometry. For all three compounds there is a deficiency of cations and the empirical formula is $M_{0.75}[Pt(S_2C_4N_2)_2]\cdot xH_2O$ (where M is Li^+ or NH_4^+) or $Mg_{0.4}[Pt(S_2C_4N_2)_2]\cdot yH_2O$.

The reflectance spectra of powdered samples were determined from 25000 to 4000 cm^{-1}. All three compounds exhibited very broad intense absorption bands below 20000 cm^{-1} but whereas the intensity of the absorption for the ammonium complex had decreased to relatively low intensity by 4000 cm^{-1} that of the lithium complex showed no decrease in intensity. The magnesium salt exhibited intermediate behaviour. These broad, intense, low energy absorptions are indicative of cooperative phenomena in the solid state and suggest that the extent of the interactions between the $[Pt(S_2C_4N_2)_2]^{n-}$ anions falls in the order $Li^+ > Mg^{2+} > NH_4^+$.

Electrical Conduction Studies

Unfortunately only the Li salt could be obtained as large enough single crystals for 4-probe measurements and measurements on the ammonium and magnesium salts had to be restricted to measurements on compressed pellets. The results for all three compounds are shown in the Table. It can be seen that the lithium salt is somewhat more conducting than the magnesium salt and both are much more conducting than the ammonium salt. This is the same order as that observed from the reflectivity studies.

Table Room Temperature Conductivity (Ω^{-1} cm^{-1})

	Compressed pellet 2-probe	Single crystal 4-probe
$Li_{0.75}[Pt(S_2C_4N_2)_2]\cdot 1.5H_2O$	10^{-2}	∿200 (max)
$NH_{40.8}[Pt(S_2C_4N_2)_2]\cdot xH_2O$	1×10^{-7}	-
$Mg_{0.4}[Pt(S_2C_4N_2)_2]\cdot yH_2O$	3×10^{-3}	-

The electrical conduction properties of the single crystals of $Li_{0.75}[Pt(S_2C_4N_2)_2]\cdot1.5\ H_2O$ have been studied in detail by 4-probe dc technique. Because of the size of the needle shaped crystals measurements could only be made along the needle axis. The conductivity along the needle axis at room temperature was found to vary from crystal to crystal and lie in the range 30 - 212 $\Omega^{-1}\ cm^{-1}$. This is a factor of 10^3 to 10^4 higher than those determined on compressed pellets. The highest values were found for freshly cropped crystals that had been allowed to dry under ambient humidity for approximately 2 hours prior to measurement. Crystals stored for weeks under conditions of ambient humidity exhibited lower values and for crystals dried over silica gel the conductivity had fallen to less than 1 $\Omega^{-1}\ cm^{-1}$. Thus the value of the conductivity is therefore very sensitive to the degree of hydration of the crystal. The maximum value of $\sigma_{\parallel}$ is similar to that found for 1-D metals such as $K_2[Pt(CN)_4]Br_{0.3}\cdot3H_2O$[9] and $(perylene)_2\ [Pt(S_2C_4N_2)_2]$[7] in the stacking axis direction.

The temperature dependence of $\sigma_{\parallel}$ has been studied over the range 292 to 30 K. For freshly cropped crystals the conductivity slowly increases with decreasing temperature and $\sigma_{\parallel}$ passes through a maximum at ~250 K. The conductivity slowly falls below 250 K and reaches the room temperature value at about 200 K. Below this temperature the conductivity falls very rapidly. Crystals stored for some time at a relative humidity of 76% showed a less pronounced maximum whilst those stored for weeks at ambient humidity exhibited a temperature independent conductivity without a maximum from room temperature down to 240 K.

The Figure shows the variation of $\sigma_{\parallel}$, normalised relative to the room temperature conductivity, with inverse temperature over the whole temperature range studied. It can be seen that the general shape of the curve is similar to that observed for KCP(Br) and related compounds.[10] At low temperatures, below 100 K, the crystal behaves as a semiconductor with an activation energy of ~34 meV.

The results described above suggest that the electrical conduction properties are very dependent on the degree of hydration of the crystal. This was confirmed by studying the temperature dependence of crystals dehydrated under vacuum at 100°C. These crystals did not display any metallic region but exhibited decreasing conductivity with decreasing temperature over the whole temperature range.

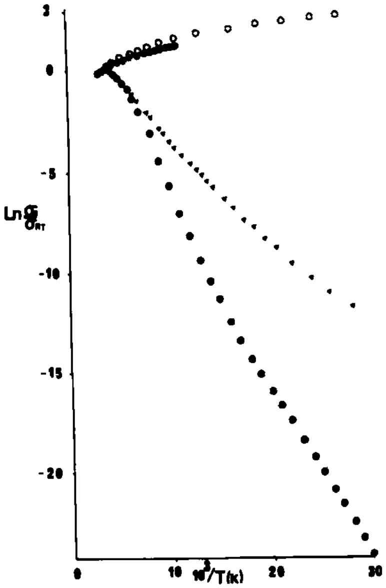
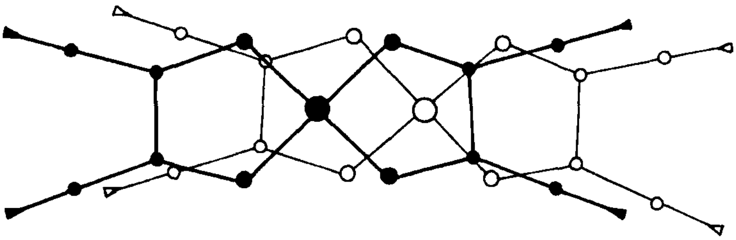


FIGURE Variation of $\mathrm{Ln}(\sigma_\parallel/\sigma_\parallel(RT))$ with inverse temperature for $Li_{0.75}[Pt(S_2C_4N_2)_2]\cdot 1.5H_2O$ ▲ ; $K_2[Pt(CN)_4]Br_{0.3}\cdot 3H_2O$[9] ●; $(\text{perylene})_2[Pt(S_2C_4N_2)_2]$[7] ○ ; and Ni(phthalocyanine)I[13] ◐ .

GENERAL DISCUSSION

The stoichiometry of these compounds suggests that they are partially oxidised $[Pt(S_2C_4N_2)_2]^{n-}$ salts and that they are analogues of the well known cation deficient tetracyanoplatinates and bis(oxalato)platinates. This is supported by the metallic conduction properties of the lithium salt just below room temperature and the high conductivity and intense low energy absorption bands found for powdered samples of both the lithium and magnesium salts.

Preliminary x-ray studies on the lithium salt indicate that the repeat distance along the conducting axis of the crystal is 3.60 Å. This is presumably the Pt-Pt separation and is very much longer than that found for KCP(Br)[11] and other 1-D metallic complexes (2.80 - 2.95 Å).[12] Previously determined structures of $[M(S_2C_4N_2)_2]^{n-}$ complexes do not contain a columnar stacked structure as in KCP(Br) but instead the anions are arranged so that they only partially overlap one another.[7,8] This can result in a short anion-anion distance even though the Pt-Pt separation is large. The type of overlap observed for the anions in (perylene)$_2$[Pt(S$_2$C$_4$N$_2$)$_2$] is illustrated below but for this compound the Pt-Pt separation is 4.19 Å.[7] A similar arrangement in Li$_{0.75}$[Pt(S$_2$C$_4$N$_2$)$_2$]•1.5H$_2$O would lead to an inter-anion separation of ∿3.2 Å.



It is clear that in these new materials the conduction pathway cannot be restricted to the platinum 5dz^2 orbitals as in the Krogmann salts and that the ligand orbitals themselves must play a very important role. In Ni(phthalocyanine)I, (Ni(Pc)I) the ligands play a dominant role and as a result this compound exhibits a radical ion ESR signal.[13] No such signal could be detected for the lithium salt down to 78 K. The temperature dependence of the conductivity is also much more similar to that of KCP(Br) than Ni(Pc)I (see Figure). An understanding of the conduction mechanism in these new materials must await further investigation but it does appear that they hold an important place intermediate between compounds whose conduction pathway is almost solely based on metal orbital overlap and those almost solely based on ligand orbital overlap.

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