

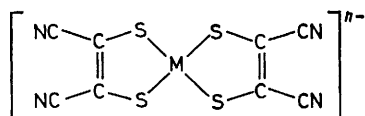
A New One-dimensional 'Metal' with Conduction through Bis(dicyanoethylenedithiolato)platinum Anions

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Summary Black needles of $\text{Li}_x[\text{Pt}(\text{S}_2\text{C}_4\text{N}_2)_2] \cdot 2\text{H}_2\text{O}$ (x ca. 0.75) exhibit a room temperature conductivity of 30–200 $\Omega^{-1}\text{cm}^{-1}$ and a temperature dependence of the conductivity similar to that of the one-dimensional metallic tetracyanoplatinate complexes such as $\text{K}_2[\text{Pt}(\text{CN})_4]\text{Br}_{0.3} \cdot 3\text{H}_2\text{O}$.

THE syntheses and electrical conduction properties of compounds containing planar $[\text{M}(\text{S}_2\text{C}_4\text{N}_2)_2]^{n-}$ ($\text{M} = \text{Ni}, \text{Pd},$ or Pt) anions have been extensively studied.^{1–4} However one-dimensional metallic properties have only been established in compounds where the organic cation and not the $[\text{M}(\text{S}_2\text{C}_4\text{N}_2)_2]^{n-}$ is responsible for the high conductivities.^{3,4}



Previous studies have concentrated on the salts of bulky cations whereas the presence of small cations in the lattice will facilitate a short intra-anion separation and hence the possibility of 1-D metallic properties being associated with the $[\text{M}(\text{S}_2\text{C}_4\text{N}_2)_2]^{n-}$ anions. The observation of a relatively high room-temperature conductivity for compressed discs of $\text{Na}[\text{M}(\text{S}_2\text{C}_4\text{N}_2)_2] \cdot 1.15\text{H}_2\text{O}$ ($\text{M} = \text{Ni}$ or Pd) supports this assertion.⁵ We report here the first observation of metallic behaviour in single crystals of a $[\text{Pt}(\text{S}_2\text{C}_4\text{N}_2)_2]^{n-}$ salts in which conduction must occur through interacting anions.

Slow aerial oxidation of a 50% aqueous acetone solution of $\text{H}_2[\text{Pt}(\text{S}_2\text{C}_4\text{N}_2)_2]$ and LiCl gave $\text{Li}_x[\text{Pt}(\text{S}_2\text{C}_4\text{N}_2)_2] \cdot 2\text{H}_2\text{O}$ (where $x = \text{ca. } 0.75$) (1) as a black microcrystalline product containing small shining black needle crystals (typical size $2.6 \times 0.13 \times 0.1$ mm). 4-Probe d.c. conduction studies were made on eight single crystals and the electrical conductivity along the needle axis (σ_{\parallel}) at room temperature

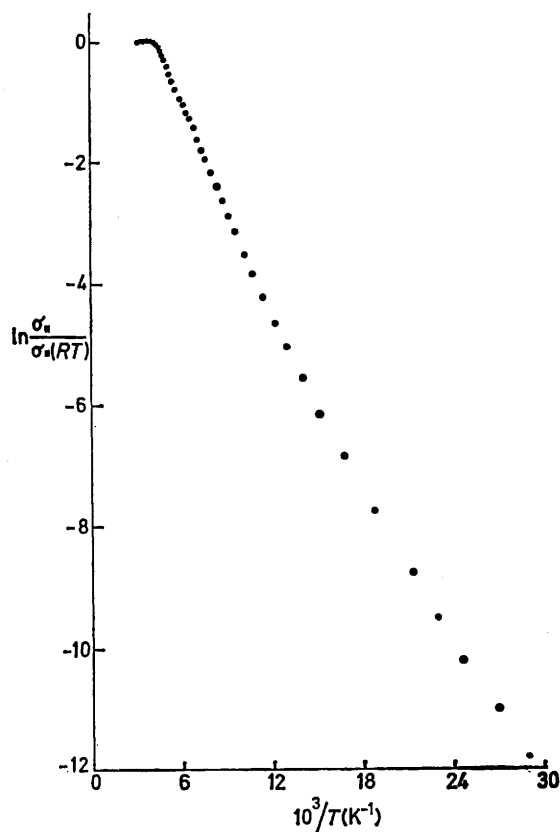


FIGURE. Variation of conductivity $\ln[\sigma_{\parallel}/\sigma_{\parallel}(RT)]$, with inverse temperature for a single crystal of $\text{Li}_x[\text{Pt}(\text{S}_2\text{C}_4\text{N}_2)_2] \cdot 2\text{H}_2\text{O}$ ($x = \text{ca. } 0.75$).

was found to vary from 30 to 200 $\Omega^{-1} \text{cm}^{-1}$ with an average value of 96 $\Omega^{-1} \text{cm}^{-1}$. The Figure shows the variation of conductivity with inverse temperature for one of these crystals. All the crystals studied showed either a small increase in conductivity, or a temperature-independent conductivity, when cooled below room temperature. This 'metallic' behaviour persisted down to *ca.* 250 K. Below this temperature the conductivity fell rapidly with decreasing temperature and below 100 K the crystals behaved as semiconductors with an activation energy of *ca.* 36 meV. The temperature dependence of the conductivity is very reminiscent of that of the 1-D metallic tetracyanoplatinate complexes such as $\text{K}_2[\text{Pt}(\text{CN})_4]\text{Br}_{0.3} \cdot 3\text{H}_2\text{O}$ ^{6,7}. The conductivity of (1) appears to be sensitive to dehydration since the conductivity of compressed pellets of (1) fell from 1.7×10^{-1} to $5 \times 10^{-3} \Omega^{-1} \text{cm}^{-1}$ after they had been heated *in vacuo* at 379 K.

The non-ionic nature of the conduction mechanism was established by charge-exhaustion experiments and therefore

(1) is the first compound in which it has been established that metallic properties arise from interacting $[\text{M}(\text{S}_2\text{C}_4\text{N}_2)_2]^{n-}$ anions.

The stoichiometry also suggests that (1) could be the first $[\text{Pt}(\text{S}_2\text{C}_4\text{N}_2)_2]^{n-}$ analogue of the cation-deficient tetracyanoplatinate or bis(oxalato)platinate 1-D metals. However, the possibility that (1) could be stoichiometric and contain as yet undetected $(\text{H}_3\text{O})^+$ in the lattice cannot be excluded.

Preliminary studies on the corresponding nickel complex indicate that it is also cation-deficient with a high conductivity and metallic-like properties at room temperature. This suggests that the complete anion and not just the metal d_{z^2} orbitals are involved in the formation of the conduction pathway.

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