Crystal Structure of a New One-dimensional Conductor $Li_{0.75}[Pt(C_4N_2S_2^{2-})_2]\cdot 2H_2O$

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The *X*-ray crystal structure analysis of $Li_{0.75}[Pt(mnt)_2]\cdot 2H_2O$ (mnt = 1,2-dicyanovinylene-1,2-dithiolato, $C_4N_2S_2{}^{2-}$) has revealed that the planar $[Pt(mnt)_2]^{n-}$ anions stack face-to-face along the *c*-axis with an eclipsed structure and with a Pt . . . Pt distance of 3.639 Å, which indicates that the conduction pathway is different from that in either the conducting organic salts of tetracyanoquinodimethane or the partially oxidised platinum-atom chain compounds.

The crystal structures, syntheses, and electrical conduction properties of compounds containing square planar $[M(mnt)_2]^{n-}$ (M = Ni, Pd, Pt) anions have been extensively studied.[1–3] Most of the studies made previously were of the salts of bulky cations[4] and these compounds were found to be semiconductors or insulators. One exception, $(perylene)_2[Pt(mnt)_2]$, (mnt = 1,2-dicyanovinylene-1,2-dithiolato, $C_4N_2S_2{}^{2-}$) exhibits metallic properties due to conduction through the organic cations.[5]

The first observation of metallic behaviour due to interacting $[Pt(mnt)_2]^{n-}$ anions was reported recently for single crystals of $Li_{0.75}[Pt(mnt)_2]\cdot 2H_2O$.[6] The conductivity along the needle axis at room temperature ($\sigma_{\|}$) determined by the 4-probe direct current technique lay in the range 30—212 Ω^{-1} cm^{-1}. The maximum values 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})[7] and $K_{1.62}[Pt(C_2O_4)_2]\cdot 2H_2O$ (*ca.* 100 Ω^{-1} cm^{-1}).[8]

Difficulties were experienced in finding single crystals suitable for the *X*-ray study and the crystal used for the *X*-ray structure analysis was twinned.

Crystal data: $Li_{0.75}[PtS_4C_8N_4]\cdot 2H_2O$, $M = 516.70$, triclinic, $P\bar{1}$, $a = 15.596(4)$, $b = 6.410(3)$, $c = 3.639(2)$ Å, $\alpha = 100.52(9)$, $\beta = 90.75(5)$, $\gamma = 96.28(6)$ °, $Z = 1$. Intensities were measured on a Rigaku automated four-circle diffractometer with Mo-K_α radiation. The structure was solved by the heavy-atom method and has been refined to a current $R = 0.058$, using 1686 reflections for which $I > 3\sigma(I)$.†

Figure 1 shows the c^* axis projection of the crystal structure of $Li_{0.75}[Pt(mnt)_2]\cdot 2H_2O$. The planar $[Pt(mnt)_2]^{n-}$ anion has a centre of symmetry at the Pt atom. The anion is close to planarity with the S atoms arranged in a square around the platinum atom and with the Pt, S(1), S(2), C(1), and C(2) atoms making a five-membered ring. The average bond lengths (in Å) are Pt–S 2.271, S–C 1.720, and C–C in the five membered ring, 1.355.

The planar $[Pt(mnt)_2]^{n-}$ anions stack face-to-face along the *c* axis with a direct overlapping. The interplanar distance between the $[Pt(mnt)_2]^{n-}$ anions is 3.592 Å and the Pt . . .Pt distance is 3.639 Å. There are no interatomic distances shorter than 3.639 Å (the length of the *c* axis) between adjacent anions within the stack. The short interatomic distances between the S atoms on adjacent molecules in adjacent stacks in the (001) plane are 3.682 and 3.743 Å.

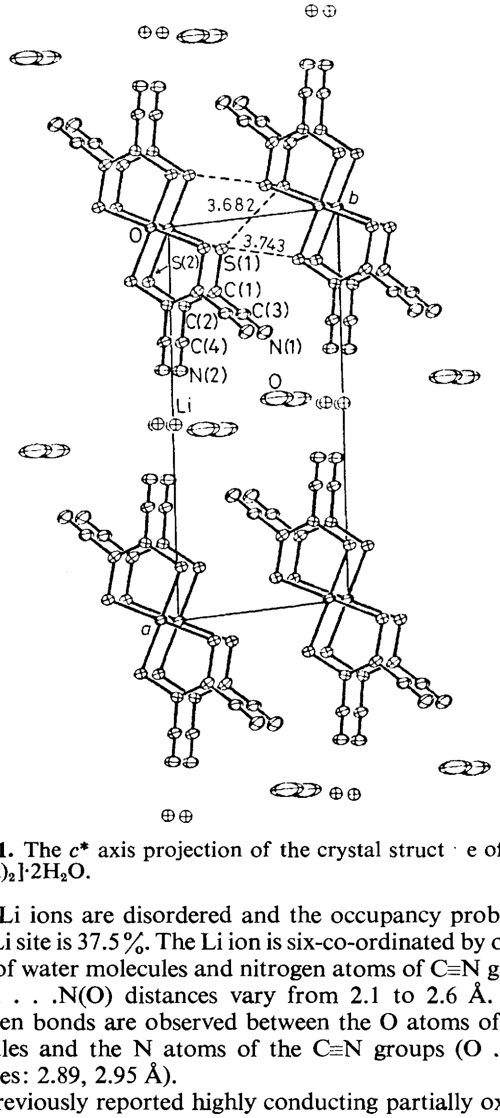

Figure 1. The c^* axis projection of the crystal structure of $Li_{0.75}$ $[Pt(mnt)_2]\cdot 2H_2O$.

The Li ions are disordered and the occupancy probability of the Li site is 37.5%. The Li ion is six-co-ordinated by oxygen atoms of water molecules and nitrogen atoms of C≡N groups. The Li . . .N(O) distances vary from 2.1 to 2.6 Å. Weak hydrogen bonds are observed between the O atoms of water molecules and the N atoms of the C≡N groups (O . . . N distances: 2.89, 2.95 Å).

In previously reported highly conducting partially oxidised platinum complexes, the metallic state is due to the formation of a partially filled band by the overlapping of the $5d_{z^2}$ orbitals of the central platinum atoms along the chain. In these compounds, a short Pt . . . Pt distance is an essential requirement for the metallic properties: $Rb_2[Pt(CN)_4](FHF)_{0.4}$, 2.80 Å;[9] $K_{1.75}[Pt(CN)_4]\cdot 1.5H_2O$, 2.97 Å;[10] $Rb_{1.67}[Pt(C_2O_4)_2]\cdot 1.5H_2O$, 2.86 Å (averaged value);[11] $Mg_{0.82}[Pt(C_2O_4)_2]\cdot 5.3H_2O$, 2.85 Å.[12] However, the Pt . . . Pt distance in $Li_{0.75}[Pt(mnt)_2]\cdot 2H_2O$ (3.639 Å) is larger than that in the Pt^{II} complex, $K_2[Pt$

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

$(CN)_4]\cdot 3H_2O$ (3.50 Å)[13] which has a conductivity of only $10^{-8}\,\Omega^{-1}\,cm^{-1}$ at room temperature.[14] Therefore, the conduction pathway cannot be formed solely by the overlap of the $5d_{z^2}$ orbitals in the Pt atoms. On the other hand, the eclipsed structure observed for the planar complexes within the stack will facilitate π-orbital overlap between adjacent molecules particularly those involving the S atoms. A similar mode of overlap with comparable inter-stack distances and room temperature conductivities has been found in some metallic tetrathiafulvalene (TTF) complexes such as $TTF.X_x$ (x = 0.7– 0.5; X = I, Br, SCN, or SeCN).[15]

The large intermolecular separation (3.592 Å) and eclipsed structure found in $Li_{0.75}[Pt(mnt)_2]\cdot 2H_2O$ shows that the conduction pathway is formed by π-orbital overlap of ligands or mixed metal–ligand orbitals in which the S atoms play an important role, and not principally through the Pt orbitals.

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