CHEMISTRY LETTERS, pp. 305 - 308, 1984. © The Chemical Society of Japan 1984

CRYSTAL STRUCTURE AND ELECTRICAL CONDUCTIVITY OF A NEW CONDUCTING BISDITHIOLATE COMPLEX $Li_{0.5}[Pt(mnt)_2]\cdot 2H_2O$

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The X-ray crystal structure analysis of $Li_{0.5}[Pt(mnt)_2]\cdot 2H_2O$ (mnt= 1,2-dicyanovinylene-1,2-dithiolato, $C_4N_2S_2{}^{2-}$) has revealed that the $[Pt(mnt)_2]^{0.5-}$ anions are stacked face-to-face along the a-axis to form a fourfold platinum chain. In contrast to the regular chain in the metallic compound $Li_{0.8}[Pt(mnt)_2]\cdot 2H_2O$, the fourfold structure can be regarded as a Peierls insulating structure. The room temperature conductivity is about 1 S cm^{-1}.

Recently a new type of one-dimensional(1-D) metallic complex containing $[M(mnt)_2]^{n-}$ (M=Ni, Pd, Pt) anions has aroused considerable interest. The first observation of metallic behavior due to interacting $[Pt(mnt)_2]^{n-}$ anions was reported for single crystals of $Li_{0.8}[Pt(mnt)_2]\cdot 2H_2O$[1,2] whose room temperature conductivity is 200 S cm^{-1}. The $[Pt(mnt)_2]^{n-}$ anions stack face-to-face with a Pt··Pt distance of 3.639 Å. This is longer than that found in the insulating Pt^{II} complex $K_2[Pt(CN)_4]\cdot 3H_2O$[3] (3.480 Å) which has the room-temperature conductivity of 10^{-8} S cm^{-1}. It is well-known that the Pt··Pt distance is shortened by the partial oxidation of the complex to form the metallic band along the Pt chain ($r_{Pt\cdot\cdot Pt}$=2.89 Å ($K_2[Pt(CN)_4]Br_{0.3}\cdot 3.2H_2O$[4]), 2.80 Å($Rb_2[Pt(CN)_4](FHF)_{0.4}$[5]), 2.96 Å($K_{1.75}[Pt(CN)_4]\cdot 1.5H_2O$[6])). The large Pt··Pt distance of $Li_{0.8}[Pt(mnt)_2]\cdot 2H_2O$ indicates that the conduction pathway is not formed by the overlap of the $5dz^2$ orbitals of the Pt atoms, but by intermolecular overlap of delocalized molecular orbitals of the whole anions in which the atomic orbitals of S in the ligands play a prominant role. Thus $Li_x[Pt(mnt)_2]\cdot nH_2O$ occupies a position in-between the 1-D platinum complexes and the sulfur donor organic metals.

Recently we have prepared conducting bisdithiolate complex $Li_x[Pt(mnt)_2]\cdot 2H_2O$. X-ray examination of the crystals revealed two types of crystals. The needle-shaped crystals have previously been identified as $Li_{0.8}[Pt(mnt)_2]\cdot 2H_2O$. We report here the crystal structure and the anisotropic electrical conductivity of the newly found elongated plate crystals $Li_{0.5}[Pt(mnt)_2]\cdot 2H_2O$.

Crystal data: $Li_{0.5}[Pt(mnt)_2]\cdot 2H_2O$, M=514.93, triclinic, $P\bar{1}$, a= 14.019(4), b= 8.423(4), c=17.137(6) Å, α= 111.86(3), β= 101.24(3), γ= 46.91(3)°, Z=4. Intensities were measured on a Rigaku automated four-circle diffractometer with Mo-Kα radiation. The structure was solved by the heavy-atom method and has been refined to a current R= 0.053, using absorption corrected 5051 reflections for which $|F_o|>3\sigma(|F_o|)$. Figure 1 shows the b*-axis projection of the crystal structure of $Li_{0.5}[Pt(mnt)_2]\cdot 2H_2O$. There are two crystallographically independent anions in the unit cell. The anions are almost planar. The S atoms are arranged in a square around the platinum atom with the Pt, S, C atoms making a five-membered ring. The average bond lengths (in Å) are Pt-S 2.266, S-C 1.705, C-C in the five membered ring, 1.389, C-C outside of the ring 1.430 and C≡N 1.133. The S-Pt-S angle is 90.2° on the average.

The $[Pt(mnt)_2]^{0.5-}$ anions are stacked face-to-face along the a-axis to form a fourfold platinum chain, and the three independent Pt··Pt distances are 3.346(2), 3.987(2), and 4.298(2) Å. In addition the tetradic unit possesses a dimeric structure, the interplanar spacing within a dimer being 3.346 Å and between dimers 3.631 Å and 3.643 Å. These interplanar distances are different from those found in the structure of the metallic complex $Li_{0.8}[Pt(mnt)_2]\cdot 2H_2O$ in which all the inter-anion distances within the column structure are equal, and from the structure of the insulating mono-anion metal dithiolate salt $Rb[Pt(mnt)_2]\cdot 2H_2O$[7] which possesses a twofold-chain containing anion dimers.

In $Li_{0.5}[Pt(mnt)_2]\cdot 2H_2O$, there are short S··S distances between anions in adjacent stacks (3.540 Å—3.589 Å) similar to those found in $Li_{0.8}[Pt(mnt)_2]\cdot 2H_2O$ and $Rb[Pt(mnt)_2]\cdot 2H_2O$. The anions are arranged along the column in a fully eclipsed configuration which is a characteristic of M_x-$[Pt(mnt)_2]$ compound containing small cations. Mono-anion salts with bulky organic cations often possess columnar stacks containing anion dimers with a staggered configuration.[8] Elemental analysis for Li cation was difficult because only a small quantity of the sample was available. The content of Li was determined as 0.5 from the refinement of the occupancy of the Li site. There are two Li sites in the unit cell which are fully occupied. The co-ordinate of Li ion is (0.1263, -0.0377, 0.4937). The Li ion is six-coordinated by oxygen atoms of water molecules and nitrogen atoms of C≡N. The Li··N(O) dis-

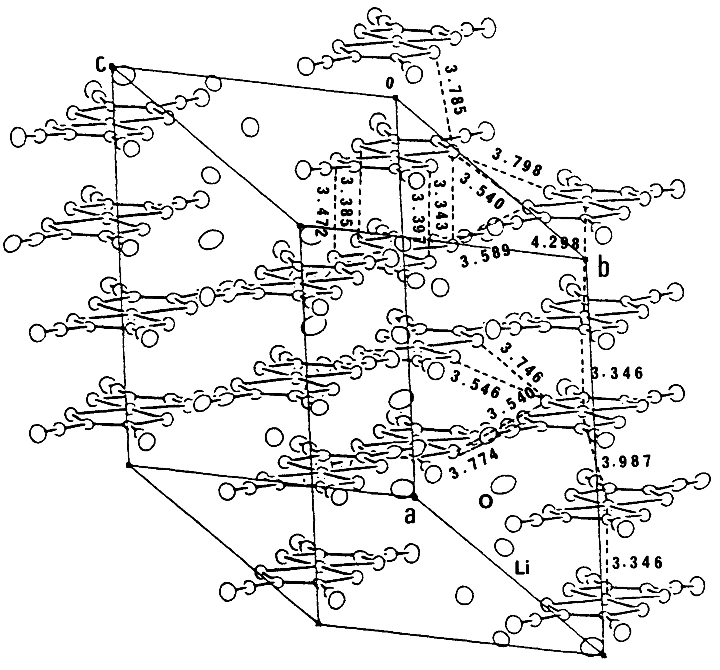

Fig. 1. The crystal structure of $Li_{0.5}$-$[Pt(mnt)_2]\cdot 2H_2O$.

tances vary from 2.127 Å to 2.629 Å. The fourfold structure of $Li_{0.5}[Pt(mnt)_2]\cdot 2H_2O$ corresponds to the $2k_F$(k_F: Fermi wave number) Peierls structure.[9] The resistivities of $Li_{0.5}[Pt(mnt)_2]\cdot 2H_2O$ were measured by 4-probe technique (Fig. 2). The room temperature conductivities along the stacking a-axis and the direction of [$\bar{1}$10] are almost the same ($\approx$1 S cm^{-1}). The small anisotropy or 2-D character of the conductivities in (001) plane is in a striking contrast to the strong 1-D character of $K_2[Pt(CN)_4]Br_{0.3}\cdot 3.2H_2O$, whose conductivity along the chain direction is 10^5 times larger than the transverse conduction. The temperature dependence of the conductivity shows the compound to behave as a semiconductor. The conductivity is lowest along the c-axis ($\approx 10^{-3}$ S cm^{-1}).

It is well-known that the electrical conductivity of 1-D platinum complexes such as tetracyanoplatinates and bis(oxalato)platinates is strongly dependent on the periodicity of the Pt chain. Similar correlation between electrical properties and the periodicity of the columns can be seen in $[Pt(mnt)_2]$ complexes. As mentioned before, $Li_{0.8}[Pt(mnt)_2]\cdot 2H_2O$ is metallic at room temperature but it undergoes metal-insulator transition at 213 K(Tc). Since the complexes are stacked regularly above Tc, the band is partially (41%) filled and 1-D metallic properties are observed. The $2k_F$ lattice distortion waves begin to develop below Tc, which open the energy gap at $k=k_F$ (k_F: Fermi wave number) and the compound transforms to a semiconducting state. In $Rb[Pt(mnt)_2]\cdot 2H_2O$, the band is half filled and a Peierls instability tends to produce a dimerization of the unit cell which is consistent with the dimer structure of $Rb[Pt(mnt)_2]\cdot 2H_2O$. Since the period of the $2k_F$ (Peierls distortion) wave is strongly commensurate with the spacing of the $Pt(mnt)_2$ complexes the band gap will be large and the electrical conductivity may be expected to be small. Experimentally the room temperature conductivity of $Rb[Pt(mnt)_2]\cdot 2H_2O$ is found to be very small ($\approx 10^{-5}$ S cm^{-1}). In the case of $Li_{0.5}[Pt(mnt)_2]\cdot 2H_2O$ the band is 1/4 filled and the Peierls distortion produce a fourfold structure with a band gap at the Fermi level resulting in semi-conducting properties which agree with the temperature dependence of the resistivity described above.

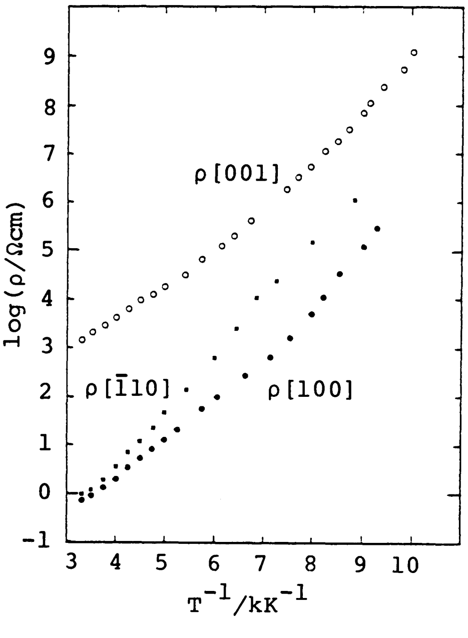

Fig. 2. The resistivity of $Li_{0.5}[Pt(mnt)_2]\cdot 2H_2O$.

Although $M_x[Pt(mnt)_2]$ has the periodicity of the stacks characteristic of 1-D conducting platinum complexes, this complex cannot be regarded as a typical 1-D conductor. In an ideal 1-D system fluctuations play an essential part and the relationship between band gap (2Δ) and the transition temperature (Tc) for a system without fluctuations $2\Delta/Tc=3.73$, cannot be applied. In addition in a 1-D system the $2k_F$ lattice distortion wave does not develop until the temperature is lowered to as low as $T \lesssim Tc/3$ ($2\Delta/Tc \gtrsim 10$ (1-D system)). However, in $Li_{0.8}$-

$[Pt(mnt)_2]\cdot 2H_2O$ the activation energy of the electrical conduction (Δ) and the transition temperature (Tc) gave the value $2\Delta/Tc$ of 3.95, which is close to the value derived from the mean field theory 3.73 and the lattice distortion developed close to Tc. The reason for the depression of fluctuations of the lattice distortion wave exists in the characteristic inter-chain transverse contacts *via* the S atoms, which are commonly observed in $M_x[Pt(mnt)_2]$ complexes. Similar transverse contacts can be also seen in the organic conductors where the S··S contacts play an essential role for the formation of the conduction pathway ($BEDT\text{-}TTF_2X$, $X=ClO_4$, PF_6..).[10] The transverse arrays of molecules observed in these conductors will afford the way to design new 2-D conductors, which will be important for the synthesis of conducting materials which do not exhibit the Peierls instability.

One of us (AEU) would like to thank the SERC and NATO (Grant No. 016.81) for support.

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(Received October 20, 1983)