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# Synthesis and Electrical Conductivity of a New Family of Pt Mixed Valence Complexes: $Pt_6(NH_3)_{14}Cl_{10}X_4$ (X=$ClO_4$, $BF_4$, and $PF_6$)

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A new family of Pt mixed valence complexes: $Pt_6(NH_3)_{14}Cl_{10}X_4$ (X=$ClO_4$, $BF_4$, and $PF_6$) was synthesized from the Magnus green salt (MGS) by the partial oxidation using an oxidant of $H_2O_2$ or by electrochemical method. On partial oxidation, the 1/6 of $Cl^-$ ligands in MGS are randomly replaced by $NH_3$ ligands and simultaneously counter ions X are introduced. These complexes comprise of one-dimensional chains with direct contact between Pt atoms and consequently a quasi-one-dimensional band made up of $5d_{z^2}$ orbital of Pt is formed. The average valence of Pt is +2.33 and the distance between Pt atoms along a chain is shorter than or comparable to that of $K_2[Pt(CN)_4]Br_{0.3}\cdot xH_2O$ (KCP). The electrical conductivity $\sigma$ of these complexes was measured from 80 K to r.t. The $\sigma$(r.t.) is rather high in spite of the measurement on the powder pressed pellets. This suggests that $\sigma$ along a chain direction may be as high as that of KCP if single crystals can be obtained. The conductivity data were fitted using a gap energy with various temperature dependence. In the complex with X=$PF_6$, there may be a phase transition caused by ordering of $PF_6^-$ ions at about 110 K.

In the last decade, many quasi-one-dimensional compounds have been synthesized and intensively studied.[1)] They comprise both organic and inorganic substances. Among organic charge transfer complexes, tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ) was most intensively studied in 1970's. TTF-TCNQ shows very high and anisotropic conductivity and shows metallic behavior down to 57 K at which it shows sharp metal-insulator(MI) transition, that is, the three-dimensional Peierls transition.[2)] Since then, many analogues of TTF-TCNQ have been synthesized to suppress the Peierls transition and to obtain metallic state or superconductivity at low temperature.[3)] Consequently, the first organic superconductor $(TMTSF)_2PF_6$ (TMTSF: tetramethyltetraselenafulvalene) was obtained, which has $T_c$ of about 1 K under a pressure of 1.2 GPa.[4)] Subsequently, $(TMTSF)_2ClO_4$, a superconductor below 1.4 K at an ambient pressure, was synthesized.[5)] Recently a new class of sulfur-based organic conductors $(BEDT\text{-}TTF)_2X$ (X=$ReO_4$, $I_3$, $IBr_2$)(BEDT-TTF: bis(ethylenedithio)tetrathiafulvalene) have been synthesized and studied intensively.[6)] At present it arrives at the stage of seeking a superconductor with higher transition temperature in organic compounds. On the other hand, in transition metal mixed valence complexes, KCP, one of Krogmann salts,[7)] was the most studied substance in 1970's.[2,8)] It shows a high and anisotropic conductivity at room temperature and shows a giant Kohn anomaly characteristic of one-dimensional compounds. But it does not show distinct transition of three-dimensional ordering to the Peierls state, because of the randomness caused by $Br^-$ which occupies 60% of the crystallographic sites and partially oxidizes Pt atoms. And it has been found that the metal dithiolates such as $Li_{0.8}[Pt(mnt)_2](H_3O)_{0.3}\cdot 1.7H_2O$[9)] (mnt: maleonitriledithiolate) and the metallomacrocycle complexes such as Ni(Pc)I[10)] (Pc: phthalocyanine) have rather high conductivity, though their conductivity is due to $\pi$ electrons. Recently, the transition metal trichalcogenide $MX_3$ and the blue bronze attract much attention from the fact that the theoretically expected Peierls–Fröhlich state is realized in these compounds.[8)] In any way, since 1980, none of transition metal complexes with conductivity due to d electrons has attracted interests. Only the third model of excitonic superconductor by KCP-like complex was proposed by W. A. Little.[11)]

As mentioned above, though KCP is a good model as the quasi-one-dimensional conductor, which comprises the quasi-one-dimensional band made up of $5d_{z^2}$ orbital of transition metal, the elucidation of its physical properties has not yet been achieved. Therefore, it will be worthwhile that the transition metal complexes with more excellent properties than KCP will be found, that is, with higher conductivity, with free of randomness and with lower temperature of the Peierls transition.

We intended to elucidate the mechanism of the MI transition in the one-dimensional conductor with $5d_{z^2}$ band, so that we planned to synthesize new substances which are free from randomness and do not contain water of crystallization which drastically changes physical properties. For the preparation of such compounds, we choose the Magnus green salt $[Pt(NH_3)_4][PtCl_4]$ (abbreviated as MGS hereafter) as a starting material, which has the columnar structure and the filled band made up of $5d_{z^2}$ orbitals of Pt atoms. Then, MGS is partially oxidized by replacing a ligand $NH_3$ or $Cl^-$ with another ligand with a different charge. Once $Pt^{2+}$ is oxidized to $Pt^{4+}$, the position vertical to the coordination plane is labile and readily coordinated by donor ligands, such as Cl, Br, I, $H_2O$, etc. Therefore, the oxidation reaction must take place in a strong acid solution without any other ligands to coordinate in order to retain the one-dimensional chain structure.[12)] Hence, the oxidation was proceeded in a $HClO_4$, $HBF_4$ or $HPF_6$ acid solution. As the result, we could obtain new mixed valence complexes of Pt; $Pt_6(NH_3)_{14}Cl_{10}X_4$ (X=$ClO_4$, $BF_4$, and $PF_6$)(hereafter abbreviated as POC, POB, and POP respectively). The synthesis, crystal structure and electrical conductivity of the complexes are reported in this paper.

## Experimental

**Preparation.** Powder of MGS is suspended in 10% $HClO_4$, $HBF_4$, or $HPF_6$ solution at room temperature and is oxidized for a few weeks by oxidant of $H_2O_2$ or by electrochemical method. Consequently, green MGS is changed to the partially oxidized salt POC, POB, or POP. They are brown with metallic luster. Partially oxidized salts thus obtained are in powder form, however, fibrous small needles crystallize from the filtrate. The acids, $HPF_6$, and $HBF_4$ are decomposed on heating so POB and POP cannot be recrystallized from these acids, while recrystallization of POC can be made from 2—40% $HClO_4$ solution. The crystals are dichroic with dark brown and colorless for polarized light parallel and perpendicular to the needle axis, respectively.

**Structure.** Though complete analysis of structure has not been achieved because of the smallness of single crystals of these three compounds, the lattice constants are determined from powder patterns of X-ray diffraction and from X-ray oscillation photographs about the needle axis as well for POC and POB. For POB, lattice constants could be determined on a four-circle diffractometer. IR spectra of POC are observed with KBr pellets.

**Electrical Conductivity.** The d.c. conductivities of pressed pellets of POC, POB, and POP prepared under pressure of 2.7—3.6×10$^8$ Pa were measured between r.t. and 80 K by the two probe method using silver paste for electrodes' contact.

In addition, thermal properties were examined using a DSC between 100 K and r.t.

## Results

Elemental analyses were carried out mainly for POC, because POC could be prepared with high purity by the recrystallization, as mentioned above. Found: H, 2.10; N, 8.77; Cl, 22.97; O, 12.06%. Calcd for $Pt_3N_7H_{21}Cl_7O_8$: H, 1.96; N, 9.07; Cl, 22.96; O, 11.84%. POC and POB were determined to be isomorphous from X-ray powder patterns. For POP, Found: H, 1.94; N, 8.41%. Calcd for $Pt_3N_7H_{21}Cl_{10}P_2F_{12}$: H, 1.81; N, 8.37%.

Table 1. Lattice Constants of POC, POB, and POP (Å)

| | POC | POB | POP |
|---|---|---|---|
| a | 15.07 | 14.917 | 6.93 |
| c | 5.62 | 5.696 | 5.78 |

POC, POB, and POP belong to tetragonal system and their lattice constants are listed in Table 1. There were no diffuse lines in oscillation photographs of POC and POB. IR spectra for POC which are consistent with the $T_d$ symmetry of $ClO_4$ suggest that $ClO_4$ is introduced not as ligand but as a counter ion. The data are listed in Table 2 together with the data from literature.[13]

The experimental results of the electrical conductivity $\sigma$ measured on heating from liquid $N_2$ temperature to room temperature are shown in Fig. 1. Conductivity maxima $\sigma_{max}$ appear at about 287 K($T_{max}$) and 273 K

Table 2. IR Spectra of POC with Respect to Molecular Vibrations of $ClO_4^-$ (cm$^{-1}$)

| POC | $Cu(ClO_4)_2 \cdot 6H_2O$ | $Cu(ClO_4)_2 \cdot 2H_2O$ | $Cu(ClO_4)_2$ |
|---|---|---|---|
| 1140 s | 1160 | 1158 vs | 1270 |
| | | | ≀ sb |
| | ≀ sb | | 1245 |
| 1104 s | | | 1130 s |
| 1090 s | 1085 | | |
| | | 1030 vs | 1030 w |
| 920 vw | 947 wsh | 920 vs | 948 s |
| | | | 920 s |
| | 800 vw | | |
| 626 m | | 660 w | 665 m |
| | | 648 s | 647 m |
| | | 626 s | 624 m |
| | | 605 s | 600 s |

$T_d$: $ClO_4^-$ $C_{3v}$: $-O-ClO_3^-$ $C_{2v}$: $\genfrac{}{}{0pt}{}{-O}{-O}\!>\!ClO_2^-$

s: strong, vs: very strong, sb: strong and broad, m: medium, w: weak, vw: very weak, wsh: weak shoulder.

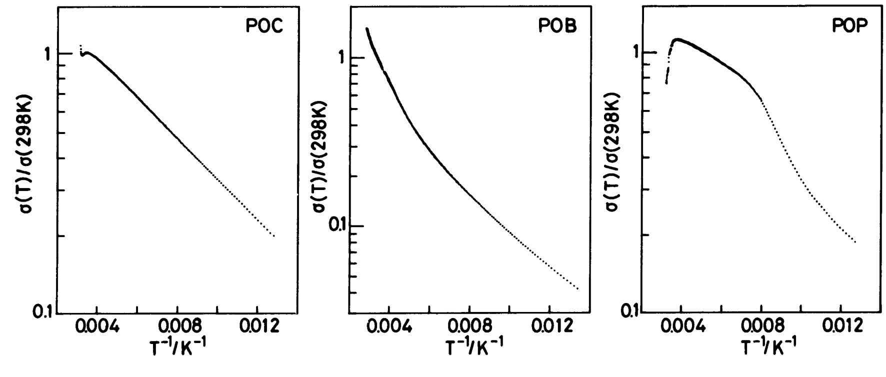

Fig. 1. Electrical conductivity of POC, POB, and POP. Conductivity normalized by the value at room temperature is plotted in a log scale against $T^{-1}$.

for POC and POP, respectively and below $T_{\mathrm{max}}$, POC and POP are semiconductive. POB is semiconductive in all temperature region observed, though a slight shoulder is observed at 276 K. If $\sigma$ in the semiconductive region is expressed as $\sigma=\sigma_0\exp(-E_a/k_BT)$, the activation energy $E_a$ becomes considerably small. They are listed in Table 3 together with the values of the conductivity at room temperature. Above $T_{\mathrm{max}}$, they are metallic in the sense of $d\sigma/dT<0$. The MI transition mentioned above takes place in temperature region rather broad as in KCP or NMP-TCNQ (NMP: *n*-methylphenazine). Above 313 K($T_{\mathrm{min}}$) for POC, $\sigma$ is again semiconductive with a rather large $E_a$ of an order of 1 eV. While, their starting material MGS is semiconductive over all temperature region with $E_a\simeq0.19$ eV.

No anomalies can be detected in thermal analyses by the DSC for MGS and its partially oxidized complexes unlike a ligand substituting mixed valence complex $Pt_6(NH_3)_{10}Cl_{10}(HSO_4)_4$ (POS) where a glass transition caused by freezing of internal rotation of substituted ligand of $HSO_4^-$ and a structural transition were observed.[14]

## Discussion

In MGS, the Pt atoms coordinated in plane by $NH_3$ and by Cl are stacked alternately and form one-dimensional chains with direct contact of Pt. In the present partially oxidized complexes, the repeating distance in the chain direction is twice of the distance between Pt atoms, retaining the periodicity of the starting material MGS. On the other hand, the averaged valence of Pt, +2.33 evaluated from the formula, suggests that the repeating distance in the chain direction is six times of the distance between Pt atoms. This implies that two of twelve Cl ligands of three molecules of MGS $-[Pt(NH_3)_4]-[PtCl_4]-[Pt(NH_3)_4]-[PtCl_4]-[Pt(NH_3)_4]-[PtCl_4]-$ are randomly replaced by $NH_3$ ligands in such a way that $NH_3$ ligands locate in positions trans to $Cl^-$ ligands, which results from a stronger trans-effect of $Cl^-$ than that of $NH_3$. Then introduced counter ions are assumed to locate between the chains and to form the hydrogen bonding with $NH_3$. The ligand substitution and the introduction of counter ions result in the partial oxidation, as the result of which 1/6 of Pt atoms changes their valence from +2 to +4 to provide a mixed valence state. The averaged valence of Pt becomes +2.33. This value itself is commensurate with the lattice unlike in KCP. Because of this partial oxidation, the distances between Pt atoms along a chain become shorter from 3.25 Å for MGS[15] to 2.81, 2.85, and 2.89 Å for POC, POB, and POP, respectively. They are comparable to or shorter than that of KCP (2.89 Å)[8] and closer to the value for Pt metal of 2.77 Å. This shrinkage of the distance between Pt atoms comes from the smallness of the substituted ligand of $NH_3$, which excludes the steric hindrance, and reflects the bare effect of the partial oxidation.

Proposed structure viewed along the chains is given in Fig. 2. The lattice parameter a for POB is smaller than that of POC. This can be explained by the difference in the bond lengths in the counter anions of 1.43 Å[16] and 1.44 Å[16] for B–F (in $BF_4^-$) and Cl–O (in $ClO_4^-$), respectively. The parameter a is twice the distance between the nearest neighbour chains. This must come from the lack of the inversion center in a tetrahedral counter anion. The disorder in a chain could not bring about such doubled periodicity. A counter anion with a $T_d$ symmetry can have two probable orientation. The difference in the orientation causes the doubled periodicity. On the other hand, for POP, in which there are octahedral $PF_6^-$ ions, the lattice constant a is the distance between the nearest neighbour chains. The bond length of P–F (1.58 Å (in $PF_6^-$))[17] is longer than those of Cl–O and B–F, but the lattice constant a is shorter than a half of those of POC and POB. POP may have a different form of packing of counter anions from that in POC and POB.

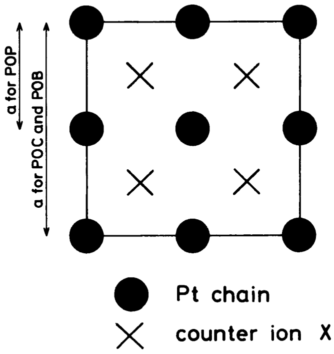

Fig. 2. Proposed structure perpendicular to the chain direction.

Table 3. Conductivity at Room Temperature and Activation Energy in Semiconductive Region for Compressed Pellets Together with the Distances between Pt Atoms

| | POC | POB | POP | POS | KCP | Pt |
|---|---|---|---|---|---|---|
| $\sigma_{\mathrm{r.t.}}$/S cm$^{-1}$ | $1.98\times10^{-2}$ | $2.20\times10^{-2}$ | $1.17\times10^{-2}$ | $2\times10^{-4}$ | $8\times10^{-2}$ [23]<br>$3\times10^{-3}$ [24] | |
| $E_a$/m eV | 16 | 28 | 10—30 | 20 | 72 | — |
| d(Pt-Pt)/Å | 2.81 | 2.85 | 2.89 | 3.25 | 2.89 | 2.775 |

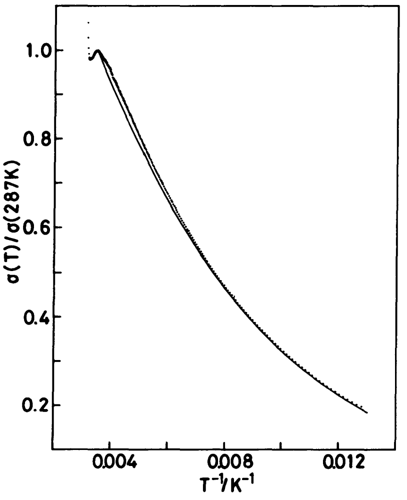

Fig. 3. Electrical conductivity of POC. Dots are the experimental data. Solid line is calculated using $\sigma = \sigma_0 \ln(1+\exp(-E_g/2k_BT))$ with $E_g=390$K (34 meV).

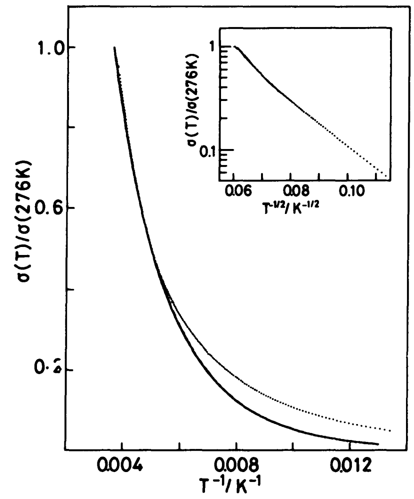

Fig. 4. Electrical conductivity of POB. Dots are the experimental data. Solid line is calculated using the gap energy with temperature dependence of $E_g(T)=E_g(0)(1-T^2/T_c^2)$, where $E_g(0)=760$K (65 meV) and $T_c=276$K. The plot of $\sigma(T)/\sigma(276\text{K})$ against $T^{-1/2}$ is shown in the inset.

Next, we will discuss the temperature dependence of the d.c. conductivity of these new mixed valence complexes of Pt. The conductivity values of the partially oxidized complexes are alike each other and rather high in spite of the measurements on the powder compressed pellets. It is surprising when we notice that the densities of electrons in conductivity of the present complexes comes from the fact that Pt atoms are partially oxidized and the distance between Pt atoms becomes shorter. The values of $\sigma$ are almost the same as that of KCP. This suggests the conductivity along the chain axis will be as high as that of KCP ($\sigma_{/\!/}=3.5\times10^2\,\text{S cm}^{-1}$ at r.t.),[18] if single crystals can be obtained. We obtained the conductivity only for compressed pellets as mentioned above, so we cannot analyse it quantitatively but may discuss its temperature dependence. The temperature dependence of these complexes differs each other. POC and POP show gradual MI transition at 287 and 273 K, respectively, and for POB at about 276 K a slight shoulder is observed in the conductivity. The MI transition mentioned above is probably the Peierls transition as in KCP. The transition temperature is higher and the activation energy is smaller than those of KCP. Though the temperature dependence of the conductivity above the transition temperature is also of interest in elucidating the nature of this transition, our data are not yet sufficient to make extensive analysis. Therefore, we will only discuss the temperature dependence below the transition temperature. Since the gap energy $E_g(=2E_a)$ is rather small and comparable to $k_BT$, we must use an explicit form of the Fermi distribution function $f(E)=1/(1+\exp(\beta(E-\zeta)))$ on calculating the number of electrons $n$ in a conduction band, where $\zeta$ is the chemical potential and $\beta=1/k_BT$. As $n$ is thought to be small, the temperature dependence in $\zeta$ is neglected. Assuming the energy independent constant density of state $N(0)$ at the conduction band, $n$ is derived to be $n=N(0)k_BT\ln(1+e^{\beta\zeta})$. When the origin of energy is taken to the bottom of a conduction band, $\zeta=-E_g/2$, where $E_g$ is the gap energy open up due to the Peierls transition. Since the conductivity $\sigma$ is expressed using relaxation time $\tau$ and effective mass $m^*$ as $\sigma=ne^2\tau/m^*$, $\sigma=\sigma_0\ln(1+\exp(-E_g/2k_BT))$ when we take $\tau\propto T^{-1}$ as in a metal. Even though there will remain the probability that random potential due to ligand substitution do randomly localize electrons in a chain. In this case $\zeta=-E_g$ is taken in the above formulation. The electrical conductivity data are usually fitted empirically using a gap energy with a various temperature dependence[14,19]; BCS-type $E_g(T)=E_g(0)(1-T/T_c)^{1/2}$, $E_g(T)=E_g(0)(1-T^2/T_c^2)$, and $E_g(T)=E_g(0)/(1+\exp(T-T_c)/T)$ and temperature dependent mobility[20] $\mu\propto T^{-\alpha}$. Then, the temperature dependent gap energy is taken as the order parameter. When there exists structural disorder in one-dimensional system, all electrons are localized at $T=0$K. Therefore, electrical conductivity can occur mainly by phonon assisted hopping. Then the conductivity can be expressed[21] as $\ln(\sigma/\sigma_0)=-(T_0/T)^{1/2}$.

For POC, $\sigma=\sigma_0\ln(1+\exp(-E_g/2k_BT))$ with temperature independent gap energy $E_g=390$ K(34 meV) gives a good agreement with experimental values as shown in Fig. 3. If the temperature dependence is introduced in the gap energy, the deviation becomes appreciable especially in higher temperature region. This temperature independence of the gap energy indicates

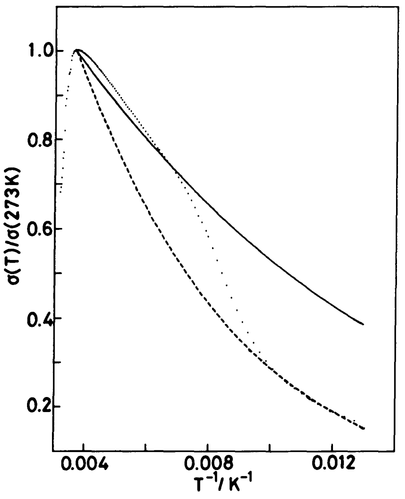

Fig. 5. Electrical conductivity of POP. Dots are the experimental data. Solid line and broken line are calculated using $\sigma=\sigma_0 \ln(1+\exp(-E_g/2k_BT))$ with $E_g$=240K (21 meV) and $E_g$=440K (38 meV) respectively.

that none of the previous forms of the gap function is applicable. Hence, the MI transition might be induced by structural phase transition, though anomaly cannot be detected in the DSC measurement. Conductivity of POB cannot be expressed in a single formula of $\sigma$. Above about 200 K, the gap energy with a temperature dependence of $E_g(T)=E_g(0)(1-T^2/T_c^2)$ gives best fit to the data, where $E_g(0)$=760 K(65 meV) and $T_c$=276 K. In the region from 77 K to 150 K, the plot of log $\sigma$ against $T^{-1/2}$ gives linear relation as shown in Fig. 4. This suggests defects or imperfections in a chain and that conductivity due to hopping is dominant at lower temperature as observed in KCP. Conductivity of POP differs considerably from those of POC and POB. There is a change in the temperature dependence at about 110 K. The temperature independent gap energy about 240 K(21 meV) above 110 K and that about 440 K(38 meV) below 140 K give best fit to the experimental results as shown in Fig. 5. A plot of $d(\ln(\sigma/\sigma_{298K}))/d(1/T)$ against $T$ shows minimum at about 110 K as shown in Fig. 6. There is a possibility that the structural phase transition takes place at 110 K. Above 110 K, counter ions $PF_6^-$ freely rotate or librate between two statistically equivalent positions, and below 110 K $PF_6^-$ ions takes a kind of ordering. Such behavior of octahedral anions is observed for $(TMTTF)_2SbF_6$ (TMTTF: tetramethyltetrathiafulvalene) at 154 K where MI transition takes place.[22]

We could synthesize a new family of transition metal complexes $Pt_6(NH_3)_{14}Cl_{10}X_4$. The conductivity is very high, though randomness cannot be excluded. Various kinds of temperature dependent conductivity are observed in these complexes. The behavior depends on the counter anions. Counter anions both

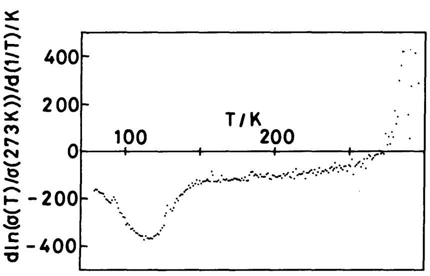

Fig. 6. Logarithmic derivation of the conductivity dln $(\sigma(T)/\sigma(273K))/d(1/T)$ plotted as a function of the temperature for POP.

tetrahedral and octahedral can be introduced by altering the acid on synthesis. The syntheses of complexes with other anions such as $ReO_4^-$ and $AsF_6^-$ are in progress. We are also trying to grow single crystals in order to make clear the crystal structure and physical properties. Furthermore, conductivity measurements with four-probe and under a high pressure are in progress in order to elucidate the gradual MI transition.

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