

## A New Redox Host for Intercalative Polymerization: Insertion of Polyaniline into $\alpha$ -RuCl<sub>3</sub>

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Lamellar nanocomposites with conductive polymers can display novel properties which can result from the molecular level interaction of the two dissimilar chemical components which comprise them. These nanocomposites have been synthesized by various intercalative methods, such as in situ redox intercalative polymerization,<sup>1,2</sup> monomer intercalation followed by polymerization,<sup>3</sup> encapsulative precipitation from solutions of exfoliated lamellar solids,<sup>4</sup> in situ oxidative polymerization coupled with encapsulative precipitation from solutions of exfoliated lamellar solids,<sup>5</sup> and other methods.<sup>6</sup> Among these, the in situ redox intercalative polymerization reaction is the most direct, and its topotactic character least disturbs the crystalline structure of the host.<sup>1c</sup> This type of reaction requires a strongly oxidizing host to provide the driving force to pull the monomers into the galleries and oxidize them into polymers. Because of the scarcity of such highly oxidizing hosts, the reaction has been limited to FeOCl,<sup>1a,c</sup> V<sub>2</sub>O<sub>5</sub>,<sup>1b,d</sup> and VOPO<sub>4</sub>.<sup>2</sup> Here we demonstrate that  $\alpha$ -RuCl<sub>3</sub> is also a suitable such host and can form an intercalative nanocomposite with polyaniline.

The lamellar structure of  $\alpha$ -RuCl<sub>3</sub> is related to that of FeCl<sub>3</sub>, which crystallizes in the defect CdI<sub>2</sub> structure

type.<sup>7</sup> Each RuCl<sub>3</sub> layer is composed of a hexagonal sheet of Ru atoms sandwiched between two hexagonal sheets of Cl atoms with ABC stacking. In the Ru sheet, one-third of the positions are left unoccupied, which leads to a honeycomb pattern and to the RuCl<sub>3</sub> stoichiometry.

Ruthenium chlorides show interesting catalytic<sup>8</sup> and photochemical<sup>9</sup> properties.  $\alpha$ -RuCl<sub>3</sub> shows intralayer ferromagnetism, interlayer antiferromagnetism,<sup>7</sup> and photoconductivity.<sup>10a</sup> Although there were only a few reports on the properties of  $\alpha$ -RuCl<sub>3</sub> before the 1990s,<sup>7,11</sup> this material has attracted increasing attention in recent years.<sup>10,12,13</sup> The intercalative properties of  $\alpha$ -RuCl<sub>3</sub>, however, have not been extensively studied except for some simple cations (e.g. Li<sup>+</sup> and Cu<sup>+</sup>) and neutral Lewis bases such as pyridine.<sup>14</sup> The intercalation of a polymer in  $\alpha$ -RuCl<sub>3</sub>, reported here, is a large step forward in exploiting the potential of this material as a host and opens up possibilities for new conductive nanocomposites.

The reaction of a solution of aniline in CH<sub>3</sub>CN with  $\alpha$ -RuCl<sub>3</sub>, in air, results in intercalative redox polymerization to polyaniline (PANI) within the gallery space of RuCl<sub>3</sub>.<sup>15</sup> The powder X-ray diffraction (XRD) patterns of the product show a 6.2 Å increase in the separation of the RuCl<sub>3</sub> layers (see Figure 1A). This expansion is reasonable for insertion of a monolayer of PANI molecules and is comparable to the 5.94 Å observed in (PANI)<sub>x</sub>FeOCl<sup>1c</sup> and 5.2 Å in (PANI)<sub>x</sub>V<sub>2</sub>O<sub>5</sub>.<sup>1b</sup> The for-

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(15) (PANI)<sub>x</sub>RuCl<sub>3</sub> was prepared by stirring 0.1 g of  $\alpha$ -RuCl<sub>3</sub> in 10 mL of 4% aniline/acetonitrile solution in open air for 1 week. The product was washed with copious acetonitrile and dried in a vacuum oven at room temperature. The composition, determined by thermogravimetric analysis (TGA) in an oxygen flow, is (PANI)<sub>x</sub>RuCl<sub>3</sub> ( $x = 0.60-0.67$ ). This result is supported by elemental analysis done by Quantitative Technologies Inc. with the following data: 15.33% C, 1.43% H, 3.11% N. The data can be translated into a formula (PANI)<sub>0.60</sub>RuCl<sub>3</sub>·0.60H<sub>2</sub>O (expected composition: 15.85% C, 1.43% H, 3.08% N).

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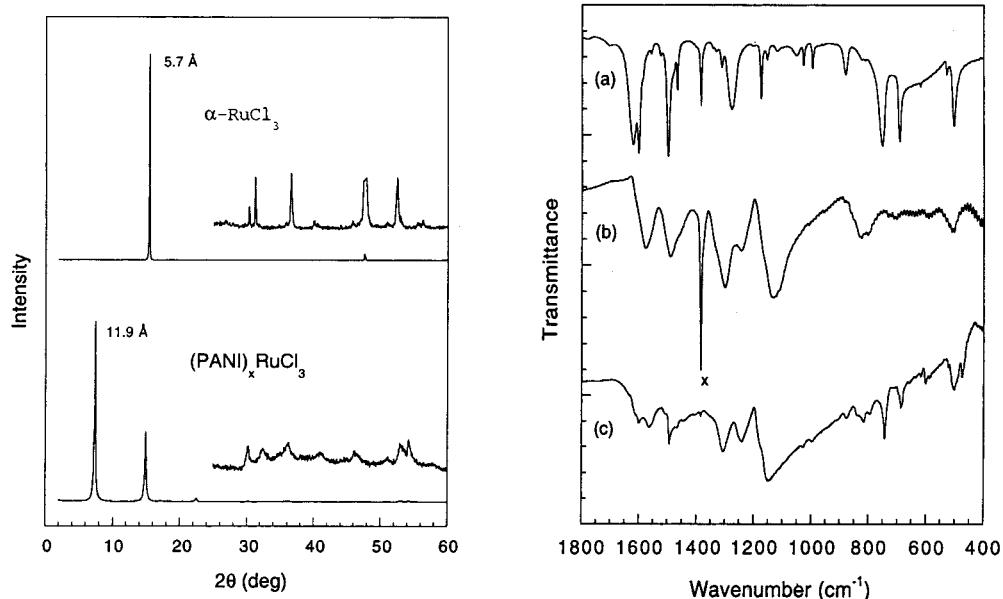
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**Figure 1.** (left) Powder XRD diagrams of  $\alpha$ - $\text{RuCl}_3$  and  $(\text{PANI})_x\text{RuCl}_3$ . (right) IR spectra of (a) aniline, (b) polyaniline, and (c)  $(\text{PANI})_x\text{RuCl}_3$ .

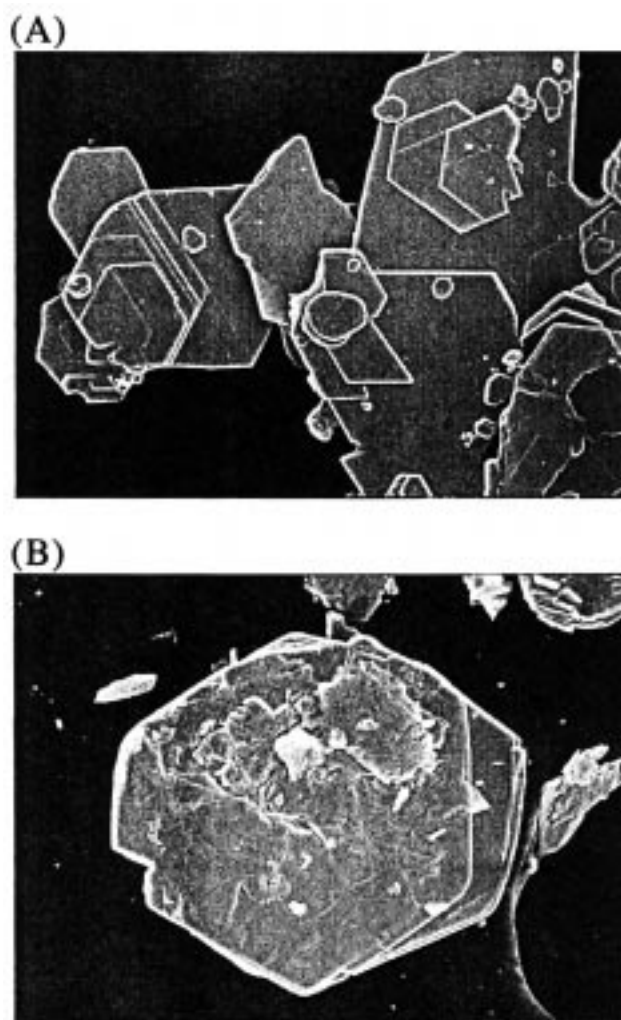
mation of polyaniline between the  $\text{RuCl}_3$  layers is supported by infrared (IR) spectroscopy (see curve c of Figure 1, right). Almost all peaks in the IR spectra of the  $(\text{PANI})_x\text{RuCl}_3$  ( $0.50 < x < 0.60$ ) are associated with polyaniline (emeraldine salt) except for a few weak peaks associated with anilinium or small oligomers (see curves a and b of Figure 1, right).

Scanning electron microscopy (SEM) images show that the size and morphology of the plates of  $(\text{PANI})_x\text{RuCl}_3$  particles are very similar to that of  $\alpha$ - $\text{RuCl}_3$  (see Figure 2), suggesting that the in situ redox intercalative polymerization reaction is topotactic and does not disrupt the structure of the host. The surfaces of the  $(\text{PANI})_x\text{RuCl}_3$  plates are rougher than those of  $\alpha$ - $\text{RuCl}_3$ , with many microcracks. Due to the much larger basal spacing of  $(\text{PANI})_x\text{RuCl}_3$ , some delamination around the edges is visible.

Thermal gravimetric analysis (TGA) measurements for  $(\text{PANI})_x\text{RuCl}_3$  done under both oxygen flow and nitrogen flow<sup>16</sup> show little weight loss in the temperature range 100–200 °C. Differential scanning calorimetry (DSC) measurements, under a nitrogen atmosphere up to 210 °C, detected no obvious thermal event until decomposition at >190 °C.

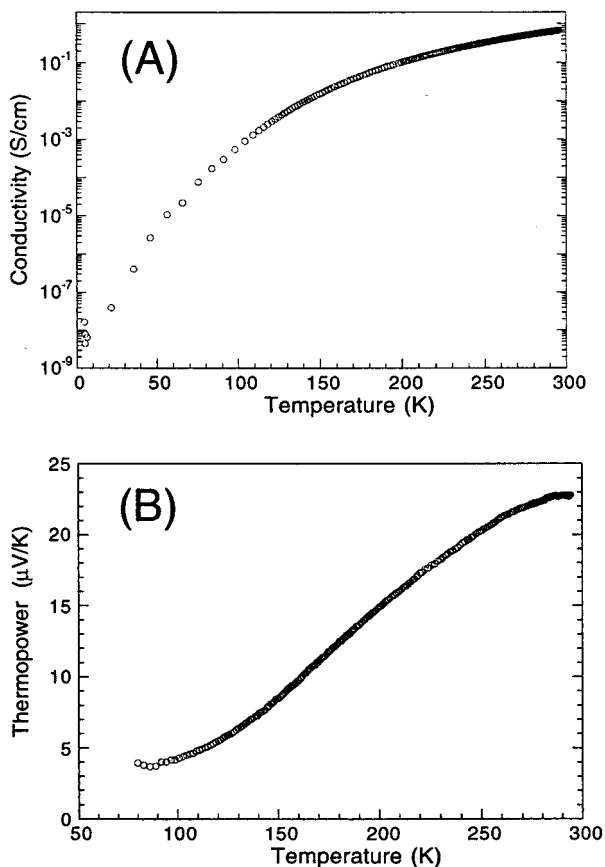
In the process of intercalation, a fraction of  $\text{Ru}^{3+}$  atoms is reduced to  $\text{Ru}^{2+}$ , resulting in a mixed valence compound. The formation of  $\text{Ru}^{2+}$  results in very stable, low-spin diamagnetic  $d^6$  centers. By virtue of the maximized ligand field stabilization energy (LFSE), this probably acts as a powerful driving force for the oxidation of aniline. Similar to the intercalative polymerization of aniline into  $\text{FeOCl}^{1c}$  and  $\text{V}_2\text{O}_5$ ,<sup>1d</sup> the presence of oxygen is key to a successful outcome of the reaction. This was verified by control experiments, where in the absence of air or oxygen no reaction occurred for 23 days.

(16) Under oxygen flow,  $(\text{PANI})_x\text{RuCl}_3$  decomposes to  $\text{RuO}_2$  when heated to 800 °C. Under nitrogen flow, both  $(\text{PANI})_x\text{RuCl}_3$  and  $\text{RuCl}_3$  continue to lose weight up to 710 °C. The total weight losses were 57.9% and 42.1%, respectively, for  $\text{RuCl}_3\cdot\text{PANI}$  and  $\text{RuCl}_3$ , forming perhaps a high metal content phase.



**Figure 2.** SEM images of (a)  $\alpha$ - $\text{RuCl}_3$  and (b)  $(\text{PANI})_x\text{RuCl}_3$ . The pictures cover an area of  $200 \times 150 \mu\text{m}$ .

The electrical conductivity of  $(\text{PANI})_x\text{RuCl}_3$  at room temperature is  $\sim 2 \text{ S/cm}$ , 3 orders of magnitude higher than that of  $\alpha$ - $\text{RuCl}_3$ ,  $5 \times 10^{-4} \text{ S/cm}$ .<sup>11c</sup> Since  $\text{Li}_x\text{RuCl}_3$



**Figure 3.** (a) Variable temperature conductivity of pressed pellet  $(\text{PANI})_x\text{RuCl}_3$ . (b) Thermopower for pressed pellet  $(\text{PANI})_x\text{RuCl}_3$ .

has only a conductivity of 0.3 S/cm, the conductivity of  $(\text{PANI})_x\text{RuCl}_3$  seems to originate from both components, i.e., by charge transport through polyaniline as well as  $[\text{RuCl}_3]^{x-}$ . By comparison, doped polyaniline (i.e. emeraldine salt) has a room-temperature conductivity of  $\sim 5\text{--}8$  S/cm. Variable temperature measurements reveal that the conductivity of pressed pellets of  $(\text{PANI})_x\text{RuCl}_3$  is thermally activated (see Figure 3a), which is due to the grain boundaries in the sample. The thermopower measurements (which are less sensitive to grain boundary effects) indicate that the material is a

hole conductor with a room-temperature Seebeck coefficient of  $\sim +22$   $\mu\text{V/K}$  (see Figure 3b). This is consistent with the fact that both the reduced  $\text{RuCl}_3$  layers as well as polyaniline (emeraldine salt) are p-type conductors.

In contrast to  $\alpha\text{-RuCl}_3$ , which shows antiferromagnetic (AF) ordering below 15.6 K,<sup>7,12a</sup>  $(\text{PANI})_x\text{RuCl}_3$  does not exhibit this transition. The disappearance of the AF transition is explained by the introduction of diamagnetic  $\text{Ru}^{2+}$  centers in the Ru sublattice and the increased separation of the  $\text{RuCl}_3$  layers. The  $(\text{PANI})_x\text{RuCl}_3$  follows Curie–Weiss law down to 10 K.<sup>17</sup> The derived Weiss constant is  $\theta = -19.5$  K, in contrast to the positive value of  $\text{RuCl}_3$ , 11.0 K,<sup>18</sup> indicating an AF exchange interaction on the average. The magnetic moment ( $\mu_{\text{eff}}$ ) for  $(\text{PANI})_x\text{RuCl}_3$  is  $1.63 \mu_{\text{B}}$ , versus  $2.32 \mu_{\text{B}}$  for  $\alpha\text{-RuCl}_3$ . The drop of the magnetic moment is due to the decrease in the number of unpaired electrons in the  $\text{RuCl}_3$  layer as the population of low spin  $\text{Ru}^{2+}$  centers increases.

In conclusion,  $\alpha\text{-RuCl}_3$  is a new host for conjugated polymer insertion via an in situ redox intercalative polymerization process. In the general class of polymer/ $\text{RuCl}_3$  nanocomposites,<sup>19</sup> the combination of the high conductivity of polyaniline and the wide-ranging catalytic properties of  $\text{RuCl}_3$ <sup>8,9</sup> could provide new materials with valuable electrocatalytic properties.

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(17) (a) An overall diamagnetic correction of  $-133 \times 10^{-6}$  emu/mol was calculated from that of  $\text{RuCl}_3$ ,  $-101 \times 10^{-6}$  emu/mol,<sup>17b</sup> and polyaniline,  $-53 \times 10^{-6}$  emu/mol-ring.<sup>17c</sup> For the best fitting of the experimental data to the Curie–Weiss Law, a  $\chi_{\text{TIP}}$  of about  $250 \times 10^{-6}$  emu/mol was used to adjust the molar magnetic susceptibility. (b) Selwood, P. W. *Magnetochemistry*, 2nd ed.; Interscience Publishers: New York, 1956; p 78. (c) Epstein, A. J.; Ginder, J. M.; Richter, A. F.; MacDiarmid, A. G. In *Conducting Polymers*; Alcácer, L., Ed.; D. Reidel Publishing Company: Dordrecht, 1986; p 121–139.

(18) When no diamagnetic adjustment was given, the derived  $\mu_{\text{eff}}$  was  $2.25 \mu_{\text{B}}$ , and the  $\theta$  was 15.8 K. The literature value was  $2.25 \mu_{\text{B}}$  and 23 K.

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