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Synthesis, characterization and thermogravimetric study of zinc and cadmium acetates–polyaniline hybrids

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Abstract

By dissolution of respective acetates and conducting polymer in dimethylformamide, homogeneous zinc acetate and cadmium acetate–polyaniline (PANI) hybrids were synthesized and characterized by infrared spectroscopy, thermogravimetry and SEM microscopy. The infrared spectra suggests that there are interactions between PANI and the metal cations involving both, imine and amine nitrogens in a typical Lewis acid–base reaction. The thermogravimetric degradation profile of the synthesized hybrids resembles those exhibited by PANI samples.

Keywords: Polyaniline; Hybrids; Acetates; Zinc; Cadmium

1. Introduction

Polyaniline (PANI) is one of the most studied conducting polymers, with many of its physical–chemical properties connected to the Brönsted acid doping process [1]. It was recently shown that PANI adsorbed on MoO_3 and As_2O_3 surfaces exerts remarkable effects on the redox processes of these oxides [2–4]. Furthermore, adsorbed PANI enhances the thermal stability of arsenic and iron oxides [5]. Polymeric blends involving PANI [6] can be prepared by dissolution of both polymers in dimethylformamide (dmf). For such blends the thermal stability is increased by increasing polyvinylchloride content. Taking into account the many possible uses of PANI [1], the possibility of doping this conducting polymer with Lewis acid species [7–9], and the remarkable properties of inorganic–organic hybrids [10], the synthesis of transition metal salts-conducting polymer hybrids is a new field in materials science. Hence, the aim of this publication is to report the synthesis, characterization and thermogravimetric study of zinc and cadmium acetates–PANI hybrids.

2. Experimental

PANI was chemically obtained from a 0.50 mol dm^{-3} solution of bidistilled aniline in a 1.0 mol dm^{-3} HCl aqueous solution. To the aniline solution maintained at 5 °C was added, dropwise for 2 h, 100 cm^3 of 0.80 mol dm^3 of $(NH_4)_2S_2O_8$ solution. After the complete addition of the oxidizing agent, the mixture was stirred for 10 h, until complete polymerization. The final polymer was washed several times with bidistilled water and acetonitrile, to remove oligomers as well any other impurities. The PANI obtained was then treated with a 1.0 mol dm^3 of NH_4OH solution to promote deprotonation.

The zinc acetate and cadmium acetate–PANI hybrids were synthesized by dissolution of both acetates (0.5 g) and conducting polymer (0.2 g) in 20 cm^3 of dmf. After mixing the solutions, 5 cm^3 of a 1.0 mol dm^{-3} HCl aqueous solution was added to promote the protonation (doping) [1] of the samples. The solvent was then slowly evaporated at room temperature in a fume hood. The obtained hybrids were dried under vacuum at room temperature for 15 h.

The pure polymer and the synthesized hybrids were characterized by FT-IR in a Bomem apparatus, with pressed KBr pellets, and thermogravimetry, in a Shimadzu TGA-50 apparatus, under argon atmosphere with a heating rate of 5 °C min^{-1}. The SEM images were obtained in a Jeol, JSM T-300 apparatus, using an accelerating voltage of 15 kV.

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3. Results and discussion

The infrared spectrum for PANI (not shown) confirms that PANI was synthesized in the emeraldine form [2,3]. As an illustrative example, the infrared spectra for zinc acetate and its respective hybrid with PANI are shown in Fig. 1. In Fig. 1(b) a superimposition of acetate and conducting polymer bands can be observed, confirming the formation of a hybrid compound. The spectrum of the ZnAc–PANI hybrid shows some bands which could be assigned as derived from PANI itself, at 1110, 950 and 690 cm^{-1}. These bands could be associated to those of free PANI [1] at 1185–1175, 1160–1180 and 780–810 cm^{-1}, respectively. However, the shifts towards lower energy values suggests some kind of interaction between PANI and the metal cation, with the possible participation of both imine and amine nitrogens, as observed for other doped samples [9]. Similar spectra were obtained for the cadmium acetate–PANI hybrid.

Scanning electron micrographs are shown in Figs. 2 and 3. As can be observed, the obtained hybrids are homogeneous (at least at the micrometer level), showing that a real hybrid, and not a mixture of two matrices was obtained. Furthermore, the elemental analysis maps (EDX) obtained for zinc and cadmium confirm that these elements are homogeneously distributed in the respective hybrid

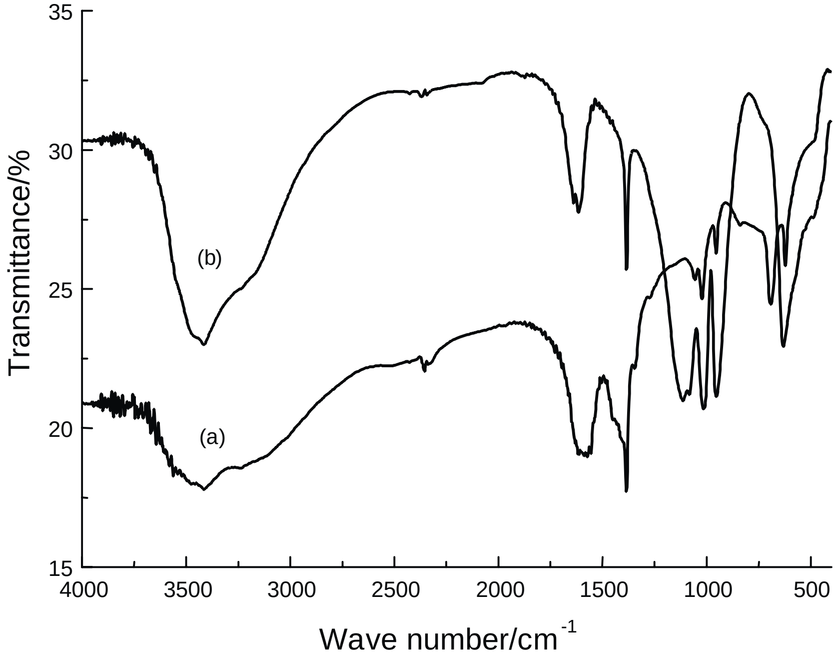

Fig. 1. Infrared spectra for zinc acetate (a) and zinc acetate–PANI hybrid (b).

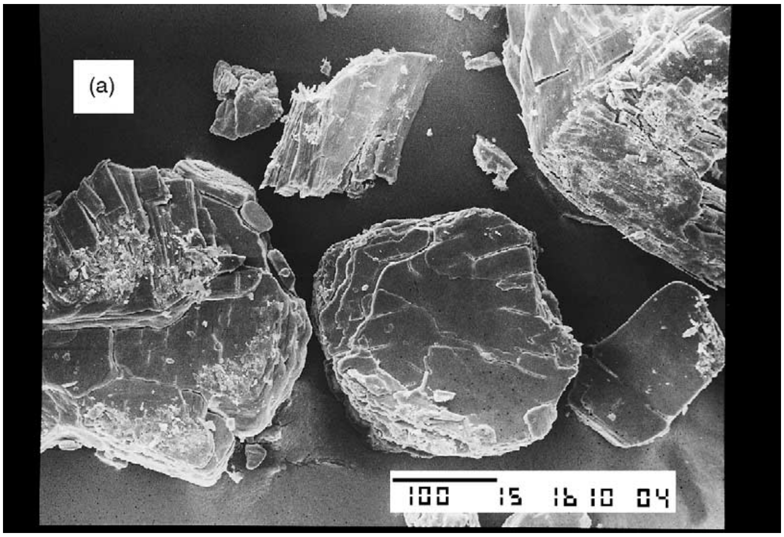

Fig. 2. SEM micrographs for zinc acetate (a) 200×, and zinc acetate–PANI hybrid (b) 1000×. The scale bar is in micrometers.

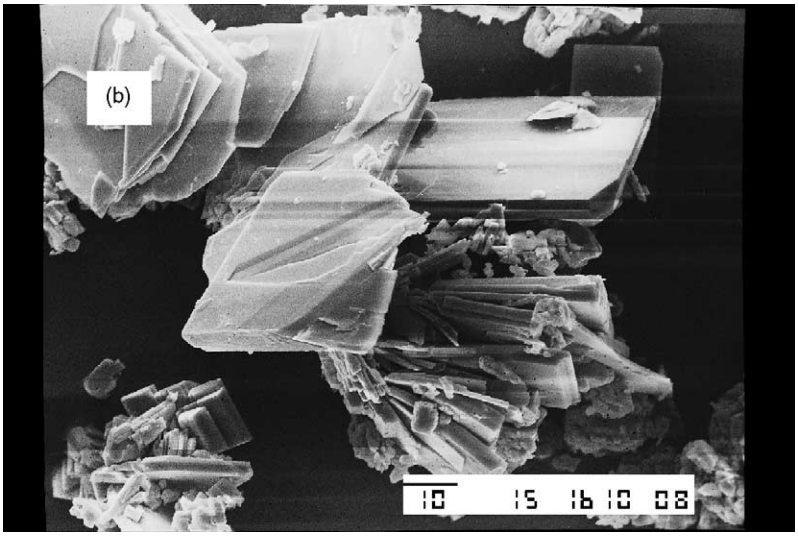

Fig. 2. (*Continued*).

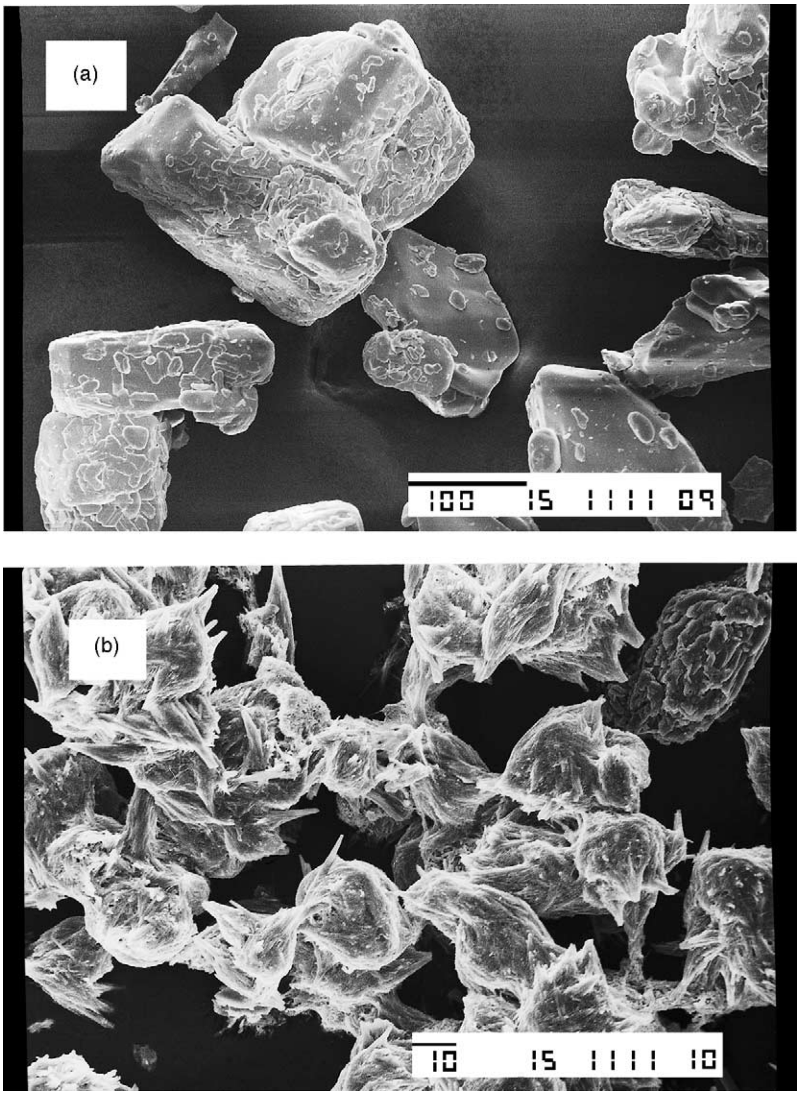

Fig. 3. SEM micrographs for cadmium acetate (a) 200×, and cadmium acetate–PANI hybrid (b) 750×. The scale bar is in micrometers.

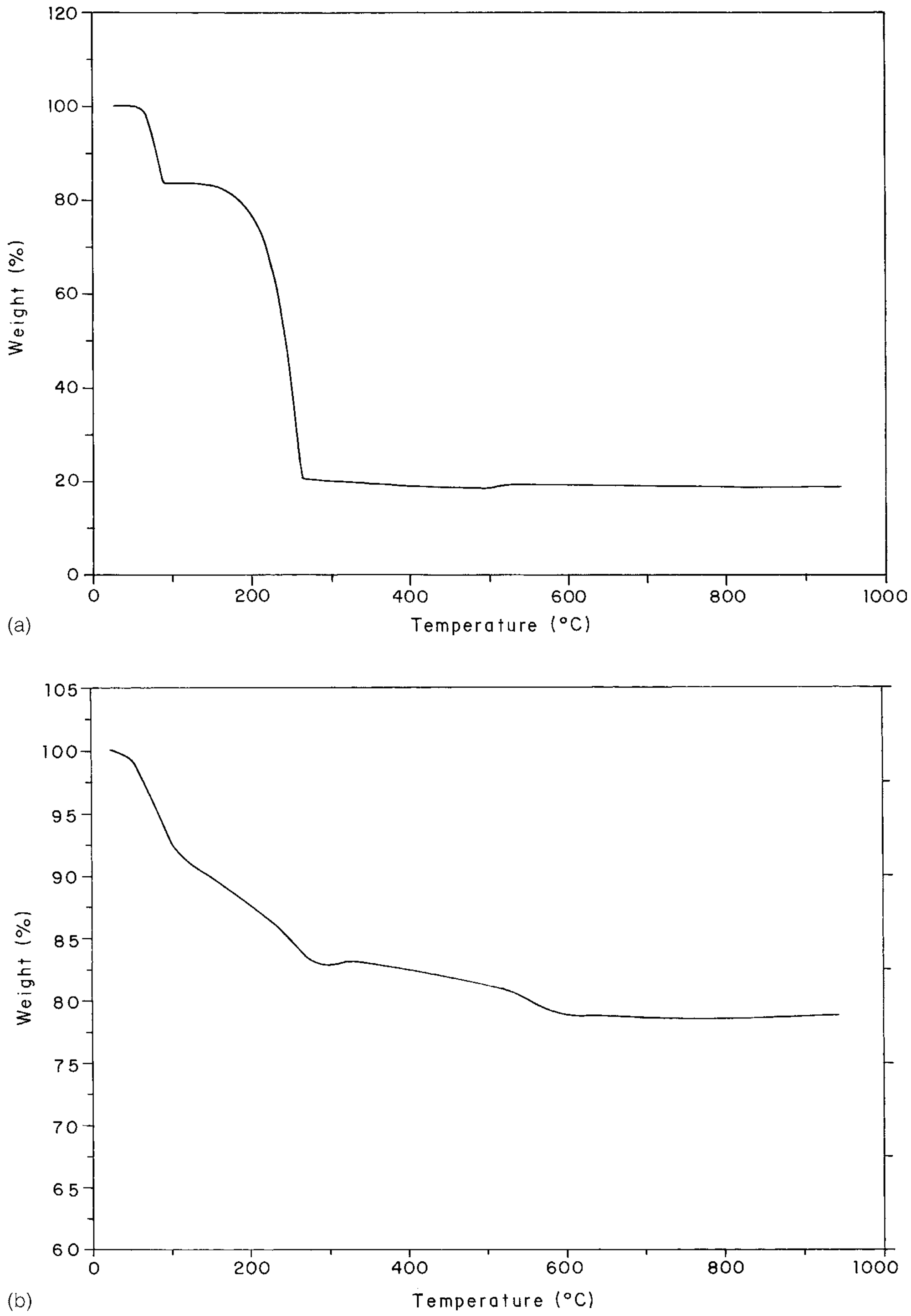

Fig. 4. Thermogravimetric curves for zinc acetate (a) and zinc acetate–PANI hybrid (b).

matrices. The Zn and Cd percentages obtained from EDX are in good agreement with the stoichiometry within a ±8 % range.

The thermogravimetric curves for the acetates and their respective hybrids are shown in Figs. 4 and 5. For zinc and cadmium acetates, Figs. 4(a) and 5(a), respectively, two distinct mass loss steps are observed. In both cases, the first mass loss step is due to the release of two water molecules, confirming the formula for the two compounds: $M(CH_3COO)\cdot 2H_2O$, M=Zn and Cd. The second mass loss is associated with the release of the organic moiety.

The thermogravimetric curve for PANI is shown in Fig. 6. A first mass loss step, below 100 °C, due to the release

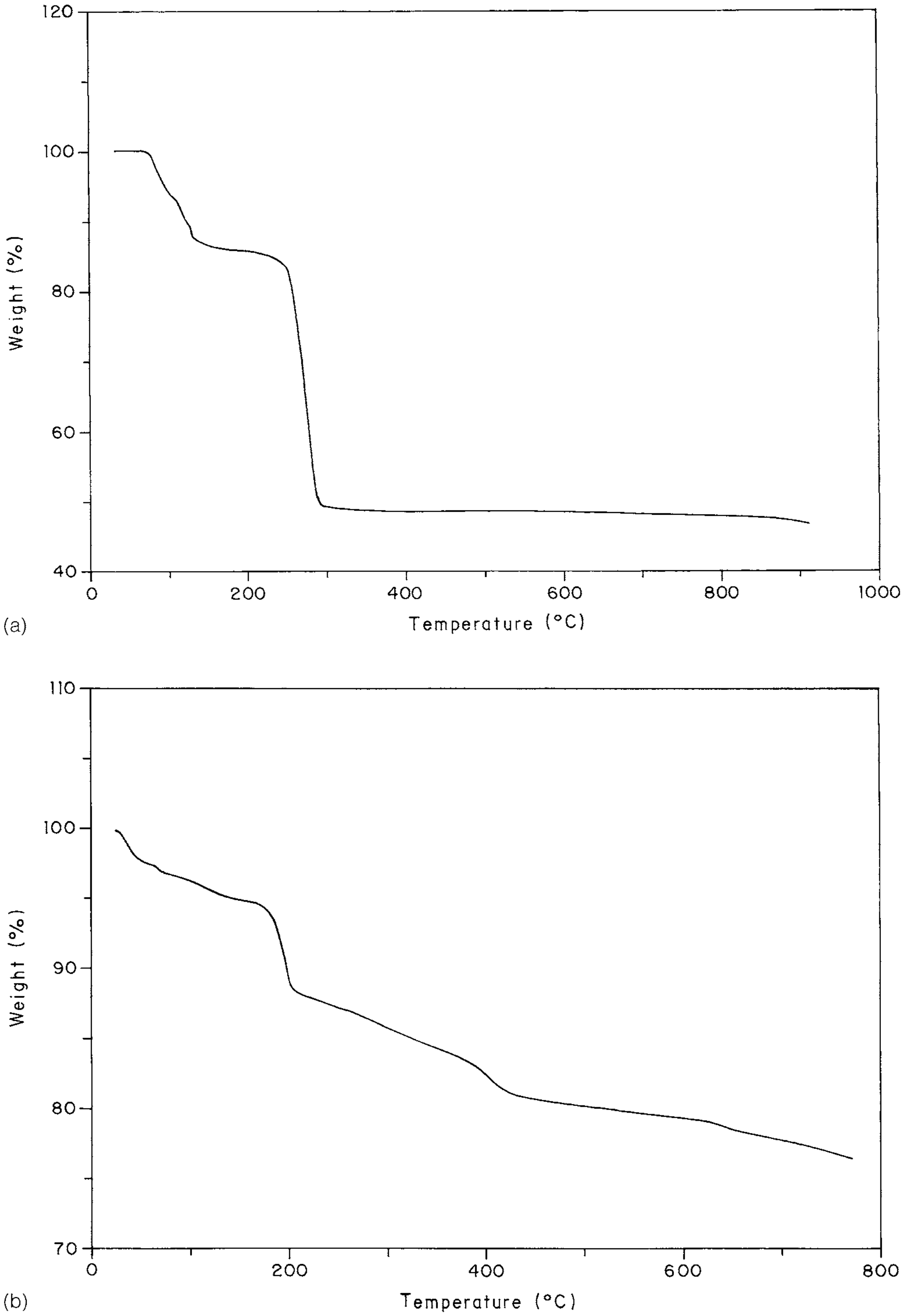

Fig. 5. Thermogravimetric curves for cadmium acetate (a) and cadmium acetate–PANI hybrid (b).

of physisorbed water molecules is observed. At 200 °C, the release of dopant molecules is taking place [11–13], followed by the thermal degradation of the organic backbone. A residue of 45%, in agreement with previously obtained results [11], for the thermal degradation of Brønsted acid doped PANI samples under inert atmospheres is observed.

Comparing Figs. 4(b) and 5(b), for zinc and cadmium hybrids, the final residue, 80 and 75%, respectively, are larger than the observed residues for the acetates: 20 and 50%, respectively. The final residue, in the of the hybrids, may be composed of PANI and acetate individual contributions and/or the resulting product of some thermally activated reaction(s).

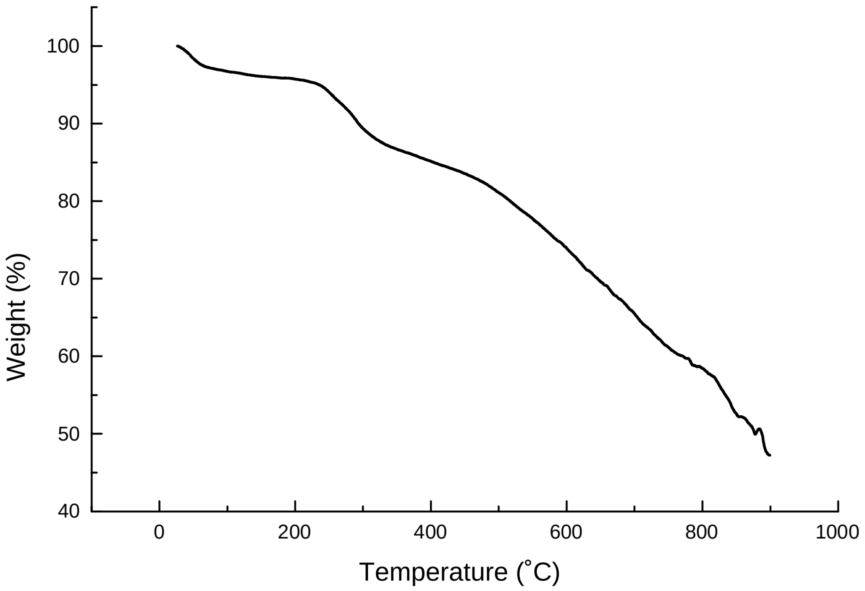

Fig. 6. Thermogravimetric curve for PANI.

4. Conclusion

The results show that

(1) Homogeneous PANI–metal acetate hybrids can be prepared through a very simple synthetic procedure.
(2) The thermogravimetric degradation profile of the hybrids resembles those exhibited by PANI samples.
(3) Chemical interactions between PANI and the metal cations, with the possible participation of both imine and amine nitrogens, could be supposed.

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