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Abstract

Ion-exchange reactions have been performed with 1D and 2D coordination polymers. 1D and 2D coordination polymers often have coordinated counterions which can be ion-exchanged for ions with either hydrogen bonding or Lewis basic sites. The 1D coordination polymer [Cu(H₂O)₃SO₄(4,4'-bpy)] and the 2D coordination network [Co(pyrazine)₂Cl₂] have been examined for their ion-exchange properties. The new ions, such as 3-pyridinesulfonate and thiocyanate, are capable of hydrogen bonding or bridging to neighboring chains or networks. The products have been characterized by PXRD, FT-IR, DR-UV-Vis, and TGA, which reveal that the materials retain their crystallinity and show replacement of the ions.

[Cu(4,4'-bipyridine)(H₂O)₃(SO₄)]¹

- 1D chain of Cu(II) and 4,4'-bipyridine with coordinated SO₄²⁻ ions.
- Often difficult to exchange SO₄²⁻, partial exchange obvious in FT-IR.
- Samples retain crystallinity upon ion-exchange.

FT-IR: Loss of SO₄²⁻ peak at ~1000 cm⁻¹ indicative of ion-exchange. In some cases, not all sulfate was removed. New peaks for exchanged ions evident for SCN⁻ and [Ag(CN)₂]⁻. Some coordination of CN from [Ag(CN)₂]⁻ evidenced by peak at 2149 cm⁻¹ and the shoulder on the C≡N peak at 2134 cm⁻¹.

PXRD: Ion-exchange results in crystalline materials with different structure than the original. In general, the *d*-spacings increase with ion-exchange, except for Cl⁻.

A **B** **C** **D**

A = [Cu(H₂O)₃(SO₄)(4,4'-bpy)] as-synthesized

B = [Cu(SO₄)(4,4'-bpy)] dehydrated

C = ion-exchanged for 3-pyridine sulfonate

D = ion-exchanged for SCN⁻

[Co(4,4'-bipyridine)(H₂O)₃(SO₄)]²

- 1D chain identical to Cu(II) chain, but different layout of chains in unit cell.
- Easily exchanges for SCN⁻ as evidenced by FT-IR.
- Samples retain crystallinity upon ion-exchange.

FT-IR: Ion-exchange is nearly complete, with no SO₄²⁻ peak at ~1000 cm⁻¹ and a new SCN⁻ peak at 2055 cm⁻¹.

PXRD: Ion-exchange modifies the crystal structure, but the material remains crystalline. Also, the *d*-spacing increases from 9.81 to 11.32 Å.

A **B**

A = [Co(H₂O)₃(SO₄)(4,4'-bpy)] as-synthesized

B = ion-exchanged for SCN⁻

[Cu(4,4'-bipyridine)(H₂O)₄](NO₃)₂

- 1D chain of Cu-bipyridine. Cu coordinated by four water molecules. No coordinated anions.
- More complete ion-exchange as evidenced by FT-IR.
- Samples retain crystallinity upon ion-exchange.

FT-IR: Exchange of NO₃⁻ (~1400 cm⁻¹) is nearly complete for both SCN⁻ and 3-pyridinesulfonate. New peak at 2092 and 2053 cm⁻¹ indicates for SCN⁻ is split due to coordination to Cu(II) centers.

PXRD: Samples retain crystallinity upon ion-exchange. Many peaks are not changed upon ion-exchange. The material exchanged for SCN⁻ is different than sample exchanged from the SO₄²⁻ 1D coordination polymer.

A **B** **C**

A = [Cu(H₂O)₄(4,4'-bpy)](NO₃)₂ as-synthesized

B = ion-exchanged for SCN⁻

C = ion-exchanged for 3-pyridine sulfonate

[Co(pyz)₂Cl₂]³

- 2D square grid of Co(II) and pyrazine, with anions (Cl⁻) above and below the layers.
- Exchange of anions could bridge between layers.
- Indication of coordination of cyanide from [Ag(CN)₂]⁻ by FT-IR analysis.

FT-IR: Ion exchange for SCN⁻ gives a new SCN⁻ peak at 2054 cm⁻¹, while retaining peaks from pyrazine (1000-1100 cm⁻¹). Likewise, exchange for [Ni(CN)₄]²⁻ yields a new cyanide peak at 2140 cm⁻¹. Both SCN⁻ and [Ag(CN)₂]⁻ have shoulders on the C≡N peak that could indicate coordination to the Co(II) of the framework.

PXRD: Ion exchange of Cl⁻ for SCN⁻ results in a known crystalline structure, Co(pyrazine)₂(SCN)₂⁴. Exchange for [Ag(CN)₂]⁻ and [Ni(CN)₄]²⁻ results in poor crystallinity and, in the case of [Ag(CN)₂]⁻, possibly little exchange.

A **B**

A = [Co(pyz)₂Cl₂]

B = ion-exchanged for SCN⁻

General Ion-exchange Procedure

- 0.10 g of the 1D or 2D coordination polymer sample was dispersed in water and a stoichiometric or 2-5 times excess of exchanging ion added to mixture as a solid. 3-pyridinesulfonic acid was dissolved in a stoichiometric amount of 0.2 M NaOH solution before addition to the coordination polymer mixture.
- Samples were stirred for 15-30 minutes at room temperature then filtered on a glass frit filter and washed with 30 mL H₂O and 30 mL of 95% ethanol. Dried samples were collected and analyzed, with typical yields ranging from 72 - 85%.

Conclusions and Future Work

- 1D and 2D coordination polymers undergo crystal-to-crystal ion-exchange at the metal center as typified by reacting [M(4,4'-bpy)]⁺² coordination polymers (M = Cu⁺², Co⁺²) or [Co(pyz)₂Cl₂]. Ions explored were for Cl⁻, SCN⁻, and 3-pyridinesulfonate.
- FT-IR analysis shows a retention of the coordination polymer backbone and a gain of incoming ion peaks.
- FT-IR analysis also shows some coordination of SCN⁻ and [Ag(CN)₂]⁻ with the coordination polymer metal ion.
- Future work will emphasize bridging between two 1D chains to build into higher dimensions. This may be through bridging ligands like SCN⁻ or [Ag(CN)₂]⁻ or through hydrogen bonding interactions.

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