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Sequestering Perrhenate with a Borate-Based Coordination Polymer: A Model for Pertechnetate Separation

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Crystals of the layered metal organic framework solid $Pb[B(Im)_4](NO_3)(nH_2O)$ can undergo exchange of the nitrate for perrhenate, a model for pertechnetate, forming $Pb[B(Im)_4](ReO_4)$. We can monitor this reaction by ^{207}Pb solid-state NMR and can isolate single crystals of the resultant material through growth in the presence of an excess of perrhenate. Such a synthetic metal–organic framework solid represents a new candidate for pertechnetate-sequestering materials.

The development of new crystalline materials using discrete molecular building blocks continues to grow rapidly, especially in the field of metal organic frameworks (MOFs).[1] Often, these materials are designed with a specific function in mind, such as a particular chemical reactivity,[2] like catalytic activity, or a physical property, like nonlinear optical behavior.[3] In most cases, the topology governs the observed attribute; the specific arrangement of component molecules in the solid state affects the desired property.[1a] This is particularly true for network MOFs that exhibit an open topology.[1c] As in open framework minerals such as zeolites or clays, the porous or layered structure of a MOF determines the type of chemistry that is observed. Recently, we reported a layered coordination polymer, $Pb[B(Im)_4](NO_3)(nH_2O)$, that exhibits chemistry similar to that observed in naturally occurring layered minerals, such as solvent intercalation and ion exchange.[4] In this report, we present the perrhenate exchange chemistry of $Pb[B(Im)_4](NO_3)(nH_2O)$, resulting in complete replacement of the nitrates with perrhenate to form $Pb[B(Im)_4](ReO_4)$ with retention of crystallinity in the network solid (Figure 1). Perrhenate is isoelectronic with the radioactive contaminant pertechnetate, TcO_4^-, and has been used to model pertechnetate separations by solid supports.[5] To the best of our knowledge, this is the first investigation of a MOF as a candidate for pertechnetate radioactive waste remediation.

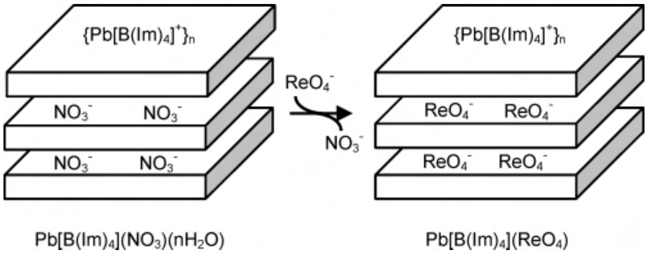

Figure 1. Schematic representation of perrhenate exchange in $Pb[B(Im)_4](NO_3)(nH_2O)$, where stoichiometric quantities of perrhenate exchange for the intralayer nitrates.

In our previous work with $Pb[B(Im)_4](NO_3)(nH_2O)$, we demonstrated that the nitrates in the intralayer spacing of the solid could be exchanged for both ^{15}N nitrate and for iodide, resulting in $Pb[B(Im)_4](^{15}NO_3)(nH_2O)$ and $Pb[B(Im)_4]I$, respectively. To evaluate the perrhenate sequestering ability of $Pb[B(Im)_4](NO_3)(nH_2O)$, we exposed crystals of this material to an aqueous solution containing a near stoichiometric (1.1 equiv) amount of $NaReO_4$ for 24 h. We used solid-state NMR (SSNMR) to monitor results from this exchange reaction. The ^{207}Pb isotope is extremely useful for SSNMR studies, with a chemical-shift range encompassing almost 8000 ppm.[6] Due to its large range, the chemical shift of the ^{207}Pb nucleus is very sensitive to changes in its immediate metal environment.[7]

Figure 2 shows the ^{207}Pb SSNMR spectrum of the $Pb[B(Im)_4](NO_3)(nH_2O)$ crystals both before and after exposure to the perrhenate solution. The broad pattern of the ^{207}Pb spectrum (~2000 ppm) results from the large chemical shift anisotropy. Under magic-angle spinning (MAS) conditions,

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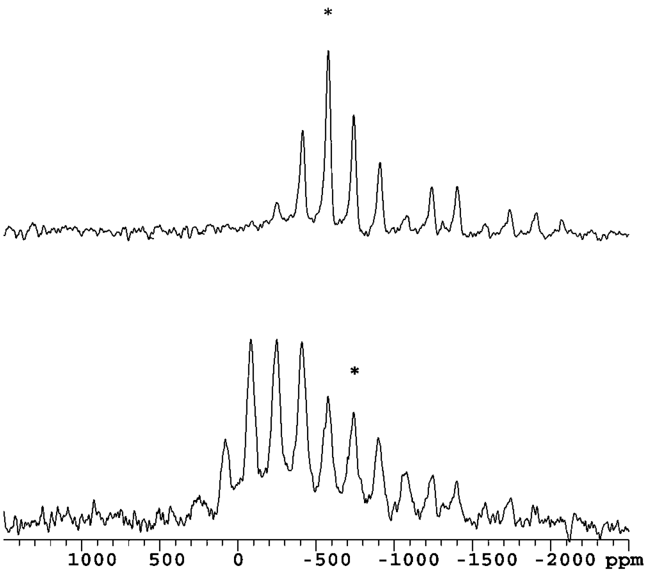

Figure 2. The ^{207}Pb SSNMR spectrum of Pb[B(Im)$_4$](NO$_3$)(1.5H$_2$O) (top) prior to exchange with 1.1 equiv of NaReO$_4$ and after exchange (bottom).

this pattern is broken up into a peak at the isotropic chemical shift, indicated with an asterisk, and a series of spinning sidebands. The changes in the overall shape of the pattern indicate that the substitution of ReO_4^- for NO_3^- does modify the electronic structure at the lead. In this study we have focused on the isotropic chemical shift of ^{207}Pb, as our previous studies have shown that this parameter is sufficient to identify anion substitution.[4] The ^{207}Pb spectrum of Pb[B(Im)$_4$](NO$_3$)(nH$_2$O) where $n = 1.5$ has an isotropic chemical shift of −533 ppm (reference, 0.5 M Pb(NO$_3$)$_2$ at −2941 ppm), determined by collecting the spectrum at several sample spinning speeds. After exposure, collection of the crystals, and washing, the material exhibits a change in isotropic chemical shift from −533 to −740 ppm. The lack of significant broadening of the peaks in the exposed spectrum is indicative of retention of crystallinity, and the chemical shift change is small and consistent with replacement of the noncoordinating nitrate with perrhenate. Similarly sized shifts are seen upon intercalation of water or exchange of other anions from between the layers of the parent Pb[B(Im)$_4$](NO$_3$)(nH$_2$O) material.[4] For example, varying degrees of hydration induce chemical shifts between −533 and −460 ppm, while replacement of the nitrate for iodide, which forms a bond with the metal, changes the chemical shift to 357 ppm. We can also monitor exchange by using infrared spectroscopy and elemental analysis. The nitrate stretch in Pb[B(Im)$_4$](NO$_3$)(nH$_2$O) appears at 1385 cm^{-1}. Upon exchange, this band disappears and is replaced by a Re−O stretching vibration at 908 cm^{-1}.[8] CHN elemental analysis also is consistent with complete exchange of nitrate for perrhenate.[9]

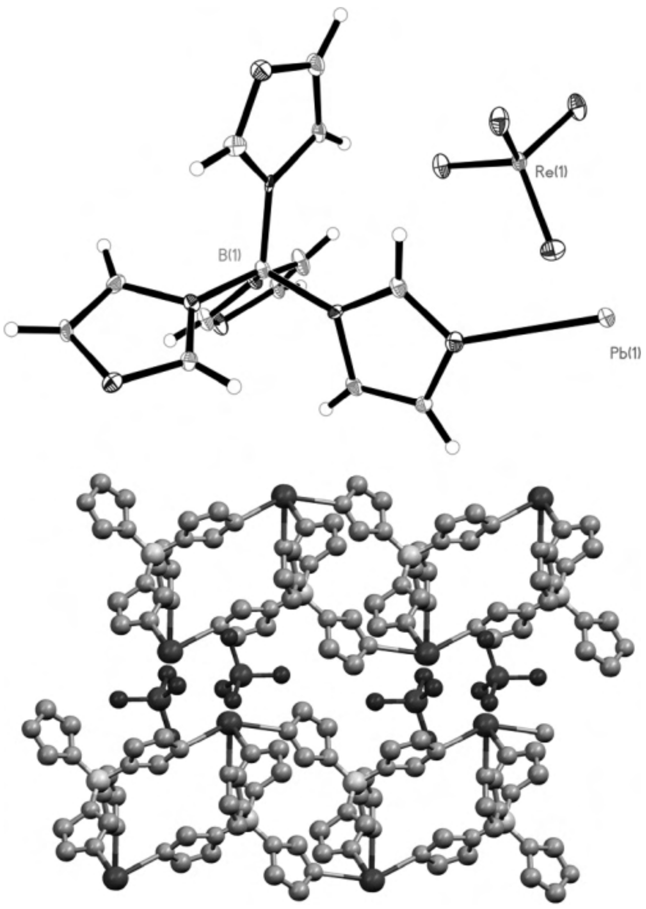

Figure 3. The asymmetric unit (top) and the extended network structure (bottom) of Pb[B(Im)$_4$](ReO$_4$). The material has the same network connectivity as in Pb[B(Im)$_4$](NO$_3$)(nH$_2$O), and the perrhenates occupy the intralayer spacing.

We were able to isolate single crystals of the exchanged material Pb[B(Im)$_4$](ReO$_4$) by growing crystals of Pb[B(Im)$_4$](NO$_3$)(nH$_2$O) in the presence of a 5-fold excess of perrhenate.[4] Single-crystal X-ray diffraction of crystals of this material resulted in elucidation of the structure of the exchanged material Pb[B(Im)$_4$](ReO$_4$). Figure 3 shows the asymmetric unit and layered network structure of Pb[B(Im)$_4$](ReO$_4$). The connectivity and stoichiometry of Pb(II) ions and tetrakis(imidazolyl)borate units are identical to that observed in Pb[B(Im)$_4$](NO$_3$)(nH$_2$O), except that in Pb[B(Im)$_4$](ReO$_4$) the nitrate has now been replaced by a noncoordinating perrhenate in the asymmetric unit void space. The extended network structure of the lead−borate layers is also identical to that seen in the parent material, and the perrhenates occupy the intralayer spacing between the lead−borate tiers. The volume of the asymmetric unit

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(9) CHN Anal. Calcd for $C_{12}H_{12}N_8B_1Pb_1Re_1O_4$: C, 19.6; H, 1.64; N, 15.2. Found: C, 19.1; H, 1.86; N, 14.9.

decreases slightly upon exchange of the perrhenate from 911.8 to 875.4 Å^3, and there are no crystallographically observed solvent water molecules in the exchanged structure. The ^{207}Pb SSNMR spectrum of crystals of Pb[B(Im)$_4$](ReO$_4$) is identical to that of the exchanged material shown in Figure 2.

In conclusion, coordination polymers that exhibit ion-exchange properties have yet to be extensively investigated as potential waste-sequestering materials. In particular, due to their positively charged lattices, MOFs can be useful for separating anionic species from aqueous solution. We are continuing this work on anion separations with Pb[B(Im)$_4$]-based solids, and future work will evaluate this material for pertechnetate separations in both simulated and actual waste samples.

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Supporting Information Available: Crystallographic information file (cif). This material is available free of charge via the Internet at http://pubs.acs.org.

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