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Construction of a Functional Layered Solid Using the Tetrakis(imidazolyl)borate Coordinating Anion

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The coordination polymer Pb[B(Im)$_4$](NO$_3$), constructed by using tetrakis(imidazolyl)borate and lead(II) nitrate solutions, is a layered material with the metal centers facing the interlayer spacing. As in naturally occurring layered minerals, this compound can readily undergo anion exchange in the solid state with retention of crystallinity. We examined stoichiometric exchange of ^{15}N-nitrate for nitrate and iodide for nitrate by ^{15}N and ^{207}Pb SSNMR and confirmed retention of crystallinity by IR and powder XRD diffraction.

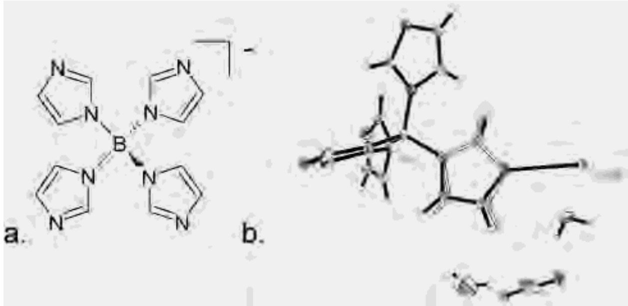

Figure 1. (a) Structure of the tetrakis(imidazolyl)borate anion and (b) the asymmetric unit of Pb(B(Im)$_4$)(NO$_3$)(1.35·H$_2$O).

The development of designed solids from discrete molecular units continues to progress rapidly, especially in the field of coordination polymers.[1] The challenges presented by this area include both the construction of robust network solids and the generation of functional materials. This work aims to control crystal design through judicious use of the molecular components and also to incorporate specific functionality determined by the composition and topology. An important attribute of functionality is the ability to bind guest molecules, such as through adsorption into pores or via intercalation between layers.[2] In this report, we present an approach for the construction of coordination polymers using the ligating anion tetrakis(imidazolyl)borate, B(Im)$_4^-$, shown in Figure 1a. In the presence of lead nitrate, this anion binds to the metal to form a layered material composed of infinite chains of Pb[B(Im)$_4$]$^+$ units. This network solid, which resembles naturally occurring layered minerals, exhibits distinct ion exchange behavior resulting from its tiered structure.

The tetrakis(imidazolyl)borate anion possesses several advantages for the construction of network solids.[3] As in carboxylate-based building blocks, borate anions can balance the charge of metal cations in resultant coordination polymer solids. With complete charge balance, problematic noncoordinating anions can be eliminated. In addition, this anion exhibits tetrahedral symmetry about the boron center and is structurally rigid, both of which encourage the growth of extended networks. Salts of this anion are quite easy to synthesize on the basis of an analogous (pyrazolyl)borate from the reaction of imidazole with borohydrides either neat or in solution at 220−230 °C.[4] We believe that this anion will be broadly useful for the construction of infinite metal-organic assemblies.

The diffusion of layered, equimolar, aqueous solutions of Na[B(Im)$_4$] and Pb(NO$_3$)$_2$ at 60 °C results in the formation of platelike white crystals of the formula Pb[B(Im)$_4$](NO$_3$)(1.35·H$_2$O). Single crystal X-ray diffraction of this material led to the elucidation of the structure of the network solid. The repeating asymmetric unit of the crystal structure with 50% thermal ellipsoids is shown in Figure 1b. The (imidazolyl)borates link the Pb cations together to form a polymeric structure, which is shown along both the *a* and *c* axes in Figure 2. All four of the imidazole rings of the borate are coordinated to a different metal center, as can be seen in the asymmetric unit. This is not initially obvious in the views of the extended solid in Figure 2 because of the overlapping

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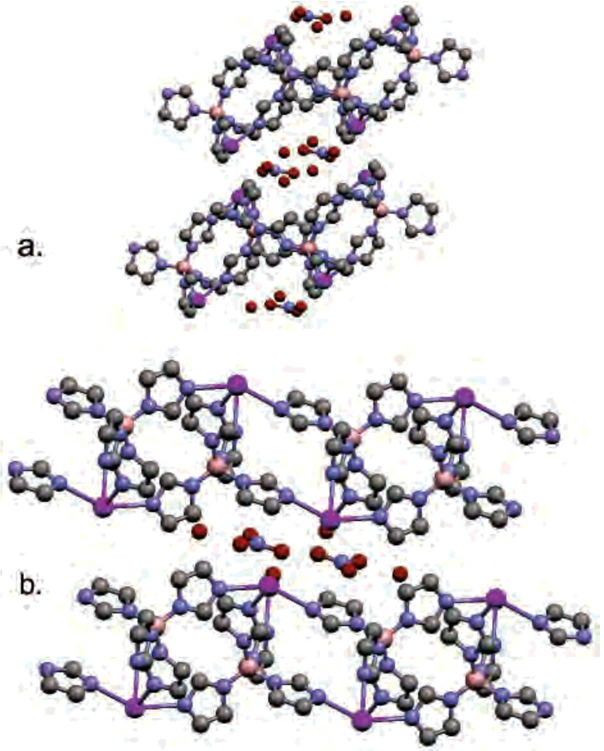

Figure 2. Extended structure of Pb(B(Im)$_4$)(NO$_3$)(1.35·H$_2$O) along the (a) *c* axis and (b) *a* axis. The lead atoms are in purple, and hydrogen atoms have been omitted for clarity.

perspective of the imidazole rings. The compound forms distinct layers, with the lead atoms directed toward the layer interface while the borates transverse the layer itself. The distance between the layers, based on the mean planes of the lead centers, is ∼3.4 Å, although edges of the peripheral imidazole rings do extend slightly farther into the layer spacing. Nitrates are found between the layers in this compound, balancing the charge of the lead cations. Solvent water is also intercalated into this material, and neither these solvent molecules nor the nitrates are directly coordinated to the lead metal centers.

In the extended solid, the lead atoms occupy positions at the layer interface (Figure 2). The lead centers are not engaged in any direct bonding interactions between the layers in this solid, and the closest distance between lead metal centers is ∼4.4 Å, much too long to be considered a bonding contact. The asymmetric coordination of lead is not unique to this material; a similar geometry about a Pb(II) ion is observed in the solid state structure of the litharge form of PbO.[5] The geometry at the lead centers conforms to the VSEPR prediction of a disphenoidal system with a stereochemically active lone pair in an equatorial position directed toward the layer interface. The presence of stereochemically active lone pairs on Pb(II) is not uncommon, but formally octahedral complexes without stereochemically active lone pairs have also been observed, such as in the Pb[(SC(NH$_2$)$_2$]$_6^{2+}$ and Pb(antipyrine)$_6^{2+}$ species.[6] Thus, the metal site at the layer interface is potentially amphoteric and could either donate its lone pair to a Lewis acid or accept an additional ligand as seen in the related coordination compound Pb(1,10-phen)$_2$(SCN)$^+$.[7] Regardless of the acid or base character of the lead, the location of the metal at the layer interface will influence the intercalation and guest absorption properties of this solid.

The presence of a layered structure in this material led us to investigate chemistry that is found to occur in minerals with a similar topology. Layered minerals, like clays and hydrotalcites, can intercalate neutral guests, exchange anions or cations, and catalyze reactions between the tiers of the solid.[2] In this report, we present investigations into the anion exchange characteristics of Pb[B(Im)$_4$](NO$_3$). Synthetic compounds are frequently probed for these described properties, and anion exchange has been observed in other recently reported materials including a Ag(I) polynitrile coordination polymer and a layered lead fluoride, Pb$_3$F$_5$NO$_3$. Compounds that can sequester anions can be used to treat contaminated industrial waste and groundwater.[8]

To examine the ability to sequester anions in Pb[B(Im)$_4$](NO$_3$), we wanted to determine if the nitrate anions could be readily exchanged. In addition, given the soft nature of the Pb(II) cation, it is expected that this material would exhibit a preference for soft anions such as iodide or bromide. The NO$_3^-$ in the interlayer region was substituted by exposing the Pb[B(Im)$_4$](NO$_3$) crystals to an aqueous solution with a mole equivalent of Na^{15}NO$_3$. After collecting the crystals by filtration, the material was characterized by ^{15}N solid state NMR (SSNMR) under magic-angle spinning conditions. The ^{15}N NMR spectrum contains two peaks at 355.4 and 353.2 ppm (Figure 3a), which were reduced to a single peak at 353.2 ppm when the crystals were washed several additional times with water (Figure 3b). Comparison with the ^{15}N NMR spectrum from solid Na^{15}NO$_3$ revealed that the peak at 355.4 ppm arises from adventitiously bound Na^{15}NO$_3$ (Figure 3c); thus, the peak at 353.2 ppm results from the intercalated nitrate ions.

The solid sample containing ^{15}NO$_3^-$ was then exposed to a mole equivalent solution of KI, collected, washed with water, and again studied by ^{15}N SSNMR. The peak at 353.2 ppm is absent (Figure 3d), showing that ion exchange has occurred with I$^-$ substituting for the nitrate anion in the layered material. Thus, complete exchange occurred with the substituting anion at stoichiometric concentrations. During both of the exchange interactions, the crystallinity of the material was not affected; powder XRD patterns of Pb[B(Im)$_4$](NO$_3$) both before and after exchange with ^{15}NO$_3^-$ and I$^-$ show no change in the degree of crystallinity, although the pattern does change upon exchange with I$^-$, as expected. In addition, IR spectra of Pb[B(Im)$_4$](NO$_3$) before and after

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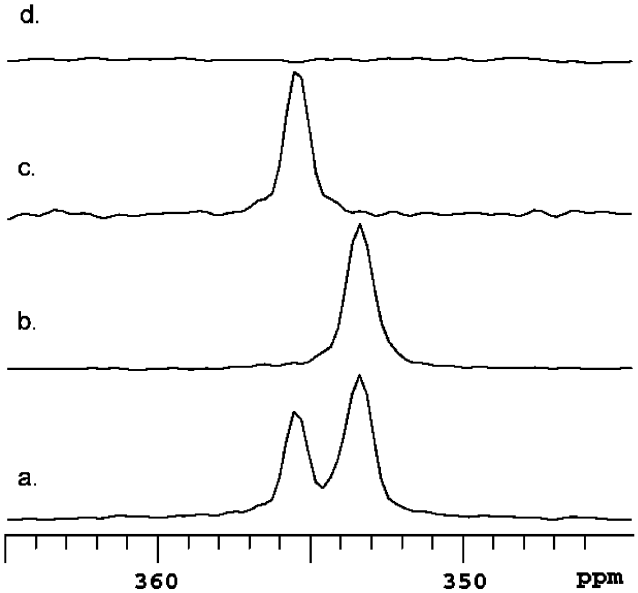

Figure 3. ^{15}N (20.5 MHz) SSNMR spectra of (a) $Pb[B(Im)_4](NO_3)$ after exposure to aqueous $Na^{15}NO_3$, (b) washed $Pb[B(Im)_4](^{15}NO_3)$ after exchange, (c) $Na^{15}NO_3$, and (d) $Pb[B(Im)_4]I$. The spinning speed was 2.7 kHz.

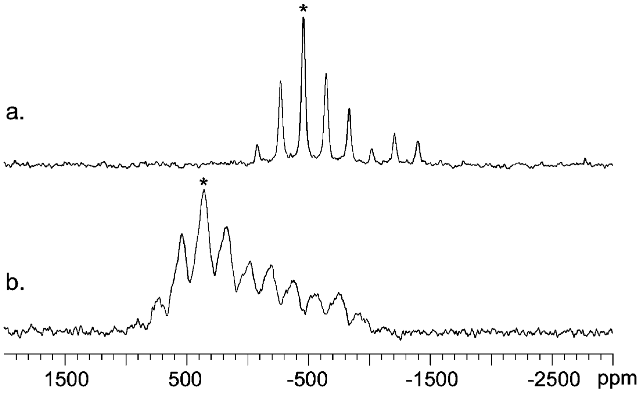

Figure 4. ^{207}Pb (42.2 MHz) SSNMR spectra of (a) $Pb[B(Im_4)](^{15}NO_3)$ and (b) Pb $[B(Im_4)]I$. The asterisk indicates isotropic chemical shift, and the spinning speed was 8 kHz.

exchange with I^- show the same fingerprint except for the loss of a peak at 1385 cm^{-1} that corresponds to the strongly absorbing nitrate vibration.

The Pb environment can also be monitored by using ^{207}Pb SSNMR (Figure 4). This isotope is ideal for SSNMR studies, with 23% natural abundance, $I = {}^1/_2$, and a chemical shift range encompassing almost 8000 ppm[9,10] that is very sensitive to changes in its local environment.[11] The ^{207}Pb spectrum of $Pb[B(Im)_4](^{15}NO_3)$ has an isotropic chemical shift of -460 ppm (reference, 0.5 M $Pb(NO_3)_2$ at -2941 ppm), determined by collecting the spectrum at several sample spinning speeds, Figure 4a. While the structure of $Pb[B(Im)_4](NO_3)$ is similar to that of the litharge form of PbO, the ^{207}Pb chemical shift for PbO is shifted downfield to 2000 ppm.[12] The change in the chemical shift results in part from the substitution of nitrogen for oxygen as the ligating atoms.

As only a single ^{207}Pb peak is observed, there is only one unique Pb environment, and the relatively narrow line widths indicate a uniform environment surrounding the lead sites. Both results are consistent with the crystalline nature of the material. The ^{207}Pb spectrum from $Pb[B(Im)_4](NO_3)$, prior to the exchange with $^{15}NO_3^-$ (data not shown), is the same as that after exchange (Figure 4a) showing that the anion substitution occurs without change to the coordination environment of the Pb nucleus. Upon substituting I^- for $^{15}NO_3^-$, the ^{207}Pb spectrum changes in both chemical shift and line width, Figure 4b. The ^{207}Pb chemical shift moves downfield to 357 ppm, a result of perturbation of the electron distribution at the Pb. This perturbation indicates an interaction between the Pb and the intercalated I^-. The broadening of the peaks, which is not a relaxation effect, likely results from slight structural heterogeneity around the Pb site induced by the presence of the I^-. It is important to note that the small change in chemical shift upon exchange with I^- indicates that no significant changes in coordination environment occur about the Pb sites, which is in agreement with the aforementioned powder XRD and IR experiments.

In conclusion, the reaction of $Pb(NO_3)_2$ and $NaB(Im)_4$ results in the formation of a layered material similar to minerals such as layered double hydroxides and talcs. The structure, which has the lead atoms at the layer interface, can readily engage in anion exchange at equivalent concentrations as shown by SSNMR. Work is in progress to explore the construction of similar materials from (imidazolyl)borates as well as probe $Pb[B(Im)_4](NO_3)$ for its ability to intercalate neutral guests and mediate organic transformations.

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Supporting Information Available: Experimental details on the NMR spectroscopy and tables of the crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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