

**Pb<sub>3</sub>F<sub>5</sub>NO<sub>3</sub>, a Cationic Layered Material for Anion-Exchange**

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**Abstract:** Our research involves the development of new cationic materials for anion-based applications. We report the solvothermal synthesis and characterization of Pb<sub>3</sub>F<sub>5</sub>NO<sub>3</sub>, a new layered lead fluoride material that, unlike the majority of layered and open-framework materials, is cationic in charge. The structure consists of polyhedral lead centers connected by doubly and triply bridging fluoride groups. We quantitatively exchanged the interlamellar nitrate groups of Pb<sub>3</sub>F<sub>5</sub>NO<sub>3</sub> for dichromate, under ambient aqueous conditions. Nuclear magnetic resonance and UV-vis spectroscopy show the reaction proceeds to 61.0% completion in several days. The material is also stable to 450 °C, which is vastly superior to organic resins that are still the standard for anion-exchange. The presence of extraframework anions also opens up other potentially unique anion-based properties, such as new catalytic reactions, anion intercalation, or growth of anionic clusters within the void spaces of the cationic material.

**Introduction**

We are focusing on the solvothermal synthesis and characterization of extended germanates, stannates, and plumbates for their potential to yield microporous zeotype materials. We use traditional cationic structure-directing agents (SDAs), such as organic amines or alkali metals, to produce extended anionic materials.<sup>1–3</sup> We are also interested in lower group 14 metals because they are larger than silicon, can have higher coordination numbers, and their polyhedra can take on smaller M–O–M bond angles.<sup>4</sup> Their connectivity should be more adaptive, leading to structures not possible with SiO<sub>4</sub>-based building blocks. We are therefore also studying anionic SDAs for the synthesis of cationic, covalently bonded, open inorganic networks that exchange, trap, or catalyze reactions of anions. Such materials would offer properties not possible with traditional microporous or layered intercalation materials that only contain extraframework cations or neutral species.

Traditional cationic SDAs have been shown to yield new layered and open-framework materials in the late group 14 metal system, where organic ammonium cations reside in the void space of these structures. A series of open-framework germanium oxides have been previously reported,<sup>5–10</sup> with several

more appearing recently.<sup>11–15</sup> Cheetham and co-workers have described a series of Sn-based extended structures, where Sn(II) centers are joined by oxalate<sup>16,17</sup> or phosphate groups.<sup>18</sup> The tin oxalates tend to be layered, as in a very recently reported ammonium tin oxalate.<sup>19</sup>

Metal phosphates and phosphonates are perhaps the most established class of 2D intercalation materials,<sup>20,21</sup> and the phosphonates have been well-studied for a wide variety of metals, including Mg, Ca, Mn, Zn, and Cd;<sup>22</sup> Ba;<sup>23</sup> and Pb.<sup>23,24</sup> Anion-exchange of the capping phosphate groups for phosphonate has been shown, but leads to a drastic reduction in the crystallinity of the starting crystals.<sup>20</sup> There exists, however, a class of synthetic and naturally occurring solids known as layered double hydroxides (LDHs). Their structures are based

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- (1) Salami, T. O.; Zavalij, P. Y.; Oliver, S. R. J. *Acta Crystallogr.* **2001**, *E57*, i49.
- (2) Salami, T. O.; Zavalij, P. Y.; Oliver, S. R. J. *Acta Crystallogr.* **2001**, *E57*, m111.
- (3) Lansky, D. E.; Zavalij, P. Y.; Oliver, S. R. J. *Acta Crystallogr.* **2001**, *C57*, 1051.
- (4) Gibbs, G. V.; Boisen, M. B.; Hill, F. C.; Tamada, O.; Downs, R. T. *Phys. Chem. Miner.* **1998**, *25*, 574.
- (5) Feng, S.; Tsai, M.; Greenblatt, M. *Chem. Mater.* **1992**, *4*, 388.
- (6) Feng, S.; Greenblatt, M. *Chem. Mater.* **1992**, *4*, 462.
- (7) Cheng, J.; Xu, R.; Yang, G. *J. Chem. Soc., Dalton Trans.* **1991**, 1537.
- (8) Jones, R. H.; Chen, J.; Thomas, J. M.; George, A.; Hursthouse, M. B.; Xu, R.; Li, S.; Lu, Y.; Yang, G. *Chem. Mater.* **1992**, *4*, 808.
- (9) Nenoff, T. M.; Harrison, W. T. A.; Stucky, G. D. *Chem. Mater.* **1994**, *6*, 525.
- (10) Roberts, M. A.; Fitch, A. N. *Z. Kristallogr.* **1996**, *211*, 378.

- (11) Cascales, C.; Gutierrez-Puebla, E.; Monge, M. A.; Ruiz-Valero, C. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 129.
- (12) Li, H.; Eddaoudi, M.; Richardson, D. A.; Yaghi, O. M. *J. Am. Chem. Soc.* **1998**, *120*, 8567.
- (13) Li, H.; Yaghi, O. M. *J. Am. Chem. Soc.* **1998**, *120*, 10569.
- (14) Li, H.; Eddaoudi, M.; Yaghi, O. M. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 653.
- (15) Cascales, C.; Gutierrez-Puebla, E.; Iglesias, M.; Monge, M. A.; Ruiz-Valero, C.; Snejko, N. *Chem. Commun.* **2000**, 2145.
- (16) Ayyappan, S.; Cheetham, A. K.; Natarajan, S.; Rao, C. N. R. *Chem. Mater.* **1998**, *10*, 3746.
- (17) Natarajan, S.; Vaidyanathan, R.; Rao, C. N. R.; Ayyappan, S.; Cheetham, A. K. *Chem. Mater.* **1999**, *11*, 1633.
- (18) See, for example: Ayyappan, S.; Cheetham, A. K.; Natarajan, S.; Rao, C. N. R. *J. Solid State Chem.* **1998**, *139*, 207. Adair, B.; Natarajan, S.; Cheetham, A. K. *J. Mater. Chem.* **1998**, *8*, 1477. Natarajan, S.; Cheetham, A. K. *J. Solid State Chem.* **1998**, *140*, 435. Liu, Y.-L.; Zhu, G.-S.; Chen, J.-S.; Na, L.-Y.; Hua, J.; Pang, W.-Q.; Xu, R. *Inorg. Chem.* **2000**, *39*, 1820 and references therein.
- (19) Audebrand, N.; Vaillant, M.-L.; Auffredic, J.-P.; Louer, D. *Solid State Sci.* **2001**, *3*, 483.
- (20) See, for example: Cao, G.; Lee, H.; Lynch, V. M.; Mallouk, T. E. *Inorg. Chem.* **1988**, *27*, 2781. Clearfield, A. *Chem. Rev.* **1988**, *88*, 125.
- (21) Thompson, M. E. *Chem. Mater.* **1994**, *6*, 1168 and references therein.
- (22) Cao, G.; Lee, H.; Lynch, V. M.; Mallouk, T. E. *Inorg. Chem.* **1988**, *27*, 2781.
- (23) Poojary, D. M.; Zhang, B.; Cabeza, A.; Aranda, M. A. G.; Bruque, S.; Clearfield, A. *J. Mater. Chem.* **1996**, *6*, 639.
- (24) Cabeza, A.; Aranda, M. A. G.; Martinez-Lara, M.; Bruque, S.; Sanz, J. *Acta Crystallogr.* **1996**, *B52*, 982.

on brucite, Mg(OH)<sub>2</sub>, which contains charge-neutral layers of edge-sharing Mg(OH)<sub>6</sub> octahedra, and each oxygen atom is bonded to three metal centers. Isomorphic substitution of  $x$  Mg<sup>2+</sup> centers for M<sup>3+</sup> centers with similar ionic radii<sup>25</sup> renders the layers cationic, with the general formula [M<sup>2+</sup><sub>1-x</sub>M<sup>3+</sup><sub>x</sub>(OH)<sub>2</sub>]-A<sup>n-</sup><sub>x/n</sub>·mH<sub>2</sub>O. There is much compositional diversity developed for LDHs: M<sup>2+</sup> = Mg<sup>2+</sup>, Fe<sup>2+</sup>, Co<sup>2+</sup>, Cu<sup>2+</sup>, Ni<sup>2+</sup>, Cd<sup>2+</sup>, or Zn<sup>2+</sup>; M<sup>3+</sup> = Al<sup>3+</sup>, Cr<sup>3+</sup>, Ga<sup>3+</sup>, or Fe<sup>3+</sup>. A range of inorganic and organic anions may be used for direct synthesis or ion-exchanged into the material, such as carbonates, halides, nitrates, sulfates, bisphosphonates, polyoxometalate anions, [Fe(CN)<sub>6</sub>]<sup>4-</sup>, porphyrins, phthalocyanines, or amino acids.<sup>26–31</sup> LDHs can also be pillared.<sup>32</sup> Despite this rich materials chemistry, all LDHs are isostructural and adopt the brucite-type double hydroxide structure.

In our exploratory synthetic work to date, we have discovered a series of materials based on late group 14 metals, which we denote BING-*n*, where BING denotes SUNY at Binghamton and *n* denotes structure type. These structures can be of any dimensionality: 1D, 2D<sup>1</sup>, and 3D<sup>2</sup> tin oxalates, layered tin phosphonates,<sup>3</sup> or the layered hexafluoro salts of germanium and tin.<sup>33</sup> Here, we describe BING-5, a cationic two-dimensional lead fluoride, its characterization, and capacity for our target application of anion-exchange.

## Experimental Section

**Synthetic Procedure.** A typical experiment involved the sequential addition of the following reagents (all used as-received) to a 250 mL Nalgene beaker, with thorough manual mixing after each step: (i) the solvent (distilled water or pyridine, Acros, 98%); (ii) concentrated HNO<sub>3</sub> (15.8 M, Fisher), if used; (iii) hydrofluoric acid, 48%; and (iv) lead(II) nitrate (Baker Inc.). The molar ratio was 80:0:1:1 or 16:2:1:1, respectively. The resultant opaque, colorless slurry was stirred mechanically for 15 min, then placed in a 23 mL capacity Teflon-lined Parr autoclave and heated statically at 150 °C for 3 days. The product was recovered by suction filtration and washed with water and acetone, with a typical yield of 61.79%.

**Characterization Methods.** Powder X-ray diffraction (PXRD) was carried out with a Scintag XDS 2000 powder diffractometer using Cu Kα radiation ( $\lambda = 1.5418$  Å), solid-state detector (which removes white radiation and  $\beta$  lines), scan range of 5° to 45° (2 $\theta$ ), and scan rate 0.5°/min. All samples were ground thoroughly in a mortar and pestle before mounting the resultant powder in the sample holder. TGA was carried out with a TA Instruments 2950, with a 10 °C/min scan rate and

**Table 1.** Summary of Crystal Data, Details of Intensity Collection, and Refinement of BING-5

empirical formula	NO <sub>3</sub> F <sub>5</sub> Pb <sub>3</sub>
formula weight	778.58
crystal size (mm)	0.37 × 0.10 × 0.008
crystal system	triclinic
space group	P1
color of crystal	colorless
<i>a</i> (Å)	7.3796(6)
<i>b</i> (Å)	12.1470(9)
<i>c</i> (Å)	16.8549(13)
$\alpha$ (deg)	100.460(2)
$\beta$ (deg)	90.076(1)
$\gamma$ (deg)	95.517(1)
<i>V</i> (Å <sup>3</sup> )	1478.6(2)
<i>Z</i>	8
<i>T</i> (K)	110(2)
<i>D<sub>c</sub></i> (g cm <sup>-3</sup> )	6.995
$\mu$ (Mo-K $\alpha$ ) (mm <sup>-1</sup> )	68.212
no. of obsd data [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	5105
<i>R</i> <sub>1</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0496
<i>wR</i> <sub>2</sub> (all data)	0.0774
goodness of fit	0.979

nitrogen purge. UV–vis absorption spectroscopy was collected on a Perkin-Elmer spectrometer, Lambda2S. NMR was carried out with a Bruker AM 360, using 10 mm broadband probe, 26.0 MHz at ambient temperature, external reference saturated NH<sub>4</sub>NO<sub>3</sub> solution in D<sub>2</sub>O + 10% HNO<sub>3</sub>, pulse width 30  $\mu$ s (~70° pulse), repetition time 0.34 s (approximate 15 × *T*<sub>1</sub>), sweep width 23809 Hz, and processing 10 Hz line broadening prior to Fourier transform. Elemental analysis was performed by Quantitative Technologies Inc. Single-crystal XRD was performed on a Bruker AXS single-crystal diffractometer with Smart Apex detector, using Mo K $\alpha$  graphite monochromated radiation ( $\lambda = 0.71073$  Å),  $\omega$ -scan, 1868 frames collected with  $\omega$  step size 0.3°, 10 s exposition time, and absorption correction for 8 $\mu$ m plates (010) using XPREP.<sup>34</sup>

## Results and Discussion

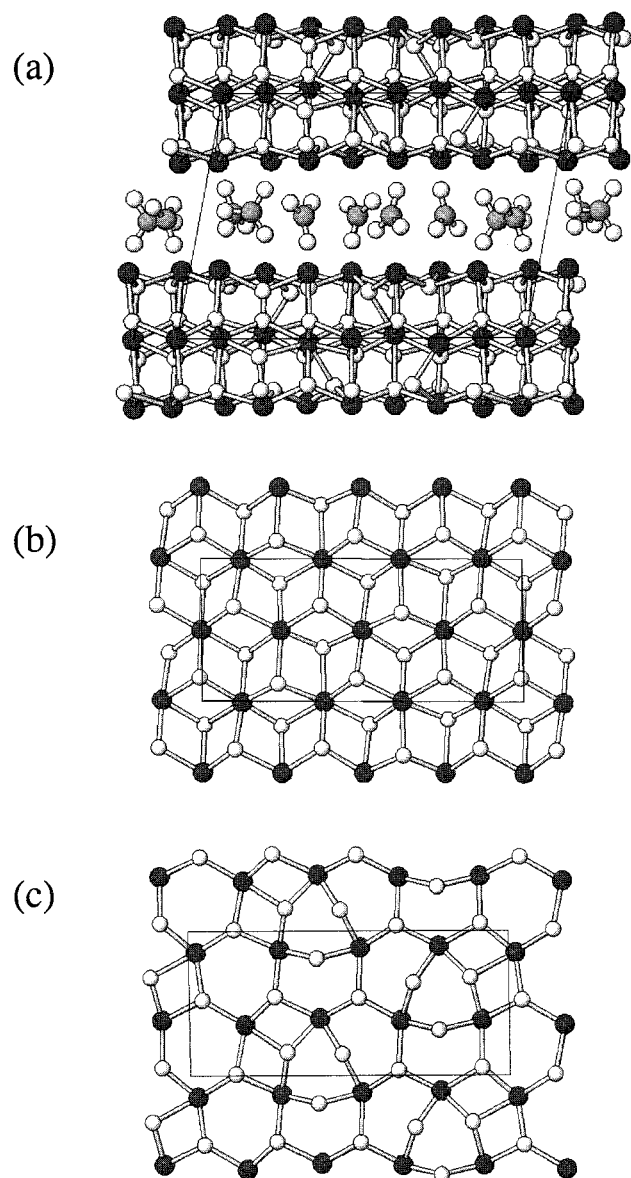
**BING-5 Synthesis and Structure.** The synthesis of this material is straightforward, and can be performed with water or pyridine as the solvent. Nitric acid must be added in the case of the latter, which leads to a synthesis mixture with a similar level of acidity. Both methods give identical products in terms of crystal size and crystallinity. The product is phase-pure, comparing the experimental PXRD pattern to the theoretical pattern based on the single-crystal data. The *d*<sub>010</sub> peak based on single-crystal data is 11.908(1) Å, while that of the as-synthesized product is 11.933(1) Å. Elemental analysis of the as-synthesized product (12.26% F, 1.35% N) also agrees well with the theoretical values based on the stoichiometric formula Pb<sub>3</sub>F<sub>5</sub>NO<sub>3</sub> (12.20% F, 1.80% N).

We initially used sodium tetrafluoroborate instead of HF<sub>(aq)</sub>, in the hope that the former would act as an anionic SDA. Instead, we obtained phase-pure BING-5, and the product is identical when NaBF<sub>4</sub> is partially or fully replaced with HF<sub>(aq)</sub>. Either act as a source of fluoride, which is necessary in order to obtain the lead fluoride material: in its absence, there was no solid product.

The structure of BING-5 consists of cationic lead fluoride [Pb<sub>3</sub>F<sub>5</sub>]<sup>+</sup> layers, separated by partially disordered interlamellar nitrate anions (Figure 1a). Three of the four crystallographically distinct nitrates were equally disordered between two positions (Table 1). Each lead fluoride layer is a triple layer, where a neutral Pb<sub>2</sub>F<sub>4</sub> layer (Figure 1b) connects to two cationic, outer

- (25) Newman, S. P.; Jones, W. Synthesis, characterization and applications of layered double hydroxides containing organic guests. *New J. Chem.* **1998**, 105.
- (26) Kooli, F.; Jones, W. Direct Synthesis of Polyoxovanadate-Pillared Layered Double Hydroxides. *Inorg. Chem.* **1995**, 34, 6237.
- (27) Hu, C. W.; He, Q. L.; Wang, E. B. Recent advances in pillaring of layered double hydroxides by polyoxometalate anion. *Prog. Nat. Sci.* **1996**, 6, 524.
- (28) Malherbe, F.; Bigey, L.; Forano, C.; de Roy, A.; Besse, J.-P. Structural aspects and thermal properties of takovite-like layered double hydroxides pillared with chromium oxo-anions. *J. Chem. Soc., Dalton Trans.* **1999**, 3831.
- (29) Beres, A.; Palinko, I.; Fudala, A.; Kiricsi, I.; Kiyozumi, Y.; Mizukami, F.; Nagy, J. B. Behaviour of Hydrotalcite and its Fe(CN)<sub>6</sub><sup>4-</sup> Pillared Derivative on Heat Treatment. *J. Therm. Anal. Calorim.* **1999**, 56, 311.
- (30) Carrado, K. A.; Forman, J. E.; Botto, R. E.; Winans, R. E. Incorporation of Phthalocyanines by Cationic and Anionic Clays via Ion Exchange and Direct Synthesis. *Chem. Mater.* **1993**, 5, 472.
- (31) Fudala, A.; Palinko, I.; Hrivnak, B.; Kiricsi, I. Amino Acid-Pillared Layered Double Hydroxide and Montmorillonite. *J. Therm. Anal. Calorim.* **1999**, 56, 317.
- (32) Komarneni, S.; Kozai, N.; Roy, R. Novel function for anionic clays: selective transition metal cation uptake by diadochy. *J. Mater. Chem.* **1998**, 8, 1329.
- (33) Kim, S. Honors Thesis, SUNY at Binghamton, Department of Chemistry, 2000.

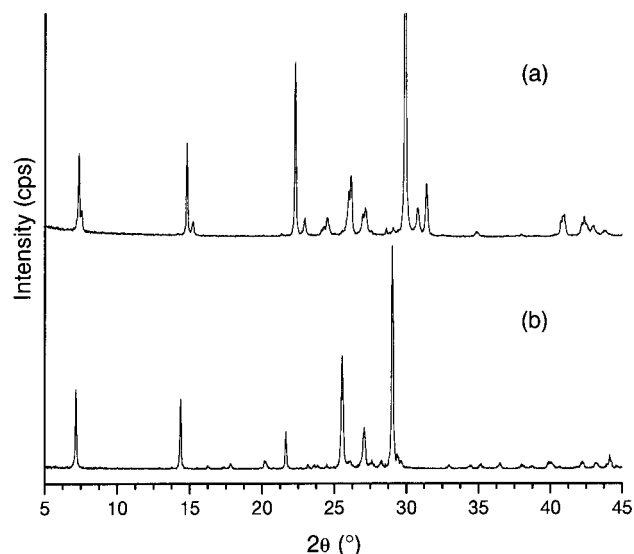
(34) Sheldrick, G. M. *SHELXL-97*; University of Göttingen, Germany, 1997.



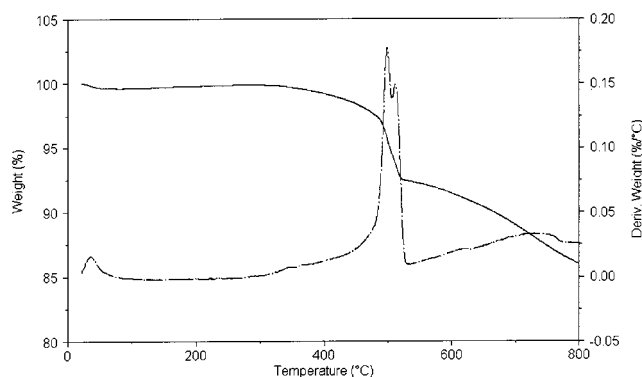
**Figure 1.** Crystallographic views of BING-5 (Pb, dark gray; N, light gray; O, F, white): (a) *a*-projection, showing the interlamellar, anionic nitrate groups; (b) *b*-projection of the neutral, central  $\text{Pb}_2\text{F}_4$  layer; and (c) one of the two outer  $[\text{Pb}_2\text{F}_3]^+$  layers that surround the  $\text{Pb}_2\text{F}_4$  layer.

$\text{Pb}_2\text{F}_3$  layers (Figure 1c), accounting for the overall formula. The lead centers are 8-coordinate cubic in the neutral central layer and 5-coordinate distorted square pyramidal in the cationic outer layers. The fluorides reside in tetrahedral sites, coordinating to four lead centers [Pb–F distances 2.319(9) to 2.810(8) Å]. The oxygens of the nitrates also interact with the outer side of the lead centers of the outer cationic layers [Pb–O distances 2.78(2) to 3.26(1) Å].

One key feature of the structure is the monovalent charge of the bridging fluoride anions that connect the metal cations into a layer. In the well-known class of zeolites and clays, the bridging anion is divalent oxygen, giving rise to anionic or neutral inorganic structures. We believe this unusual feature of BING-5 is a consequence of the large radius and softness of the lead atoms, and we are attempting to use other metals in a similar manner. The nitrate groups charge-balance the layers, fill the empty space, and stabilize the structure, as for zeolite structure-directing agents, but happen to be negative in charge.



**Figure 2.** PXRD patterns: (a) as-synthesized BING-5 material and (b) after anion-exchange for 3 days, showing the open structure remains intact.



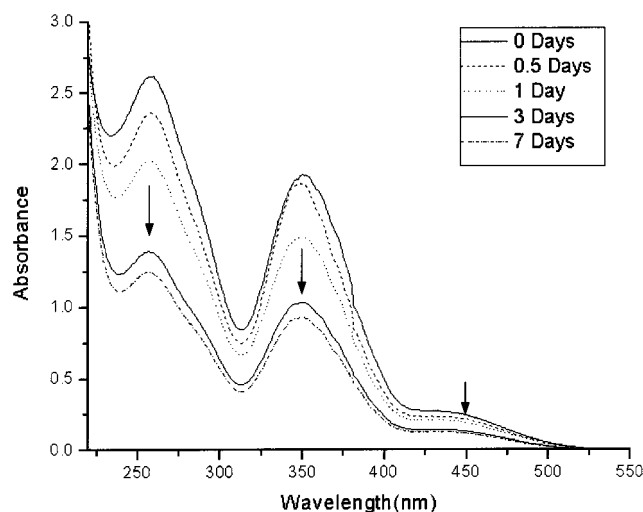
**Figure 3.** The TGA trace of BING-5 shows that the material is stable to approximately 450 °C.

**Characterization of BING-5.** The PXRD pattern of the product, which consisted of large, colorless plates, displays high crystallinity, phase purity, and a layer-to-layer distance of 12.151(2) Å (Figure 2a). TGA studies showed that BING-5 retains its structure to ca. 450 °C (Figure 3), where subsequent PXRD indicated it decomposed to  $\alpha\text{-PbF}_2$ . This stability is due to the strong Pb–F covalent bonding network within the layers, the electrostatic bonding with the interlamellar nitrates, and the close contact of the lead centers with one oxygen of the nitrates (see above).

**Anion-Exchange.** In this procedure, we simply place a known amount of material in solution and stir for a desired amount of time.<sup>35</sup> PXRD of a sample of BING-5 crystals after exchange indicates the material retains an open structure (Figure 2b, cf. Figure 2a). We were unable to index the pattern, but found that the  $d_{010}$  peak increased slightly to 12.298(1) Å.

We found that pre-ground material absorbs dichromate, releasing interlamellar nitrate, but gradually decomposed to lead chromium oxide ( $\text{PbCrO}_4$ , crocoite) over a period of 7 days.

(35) A 1.0 mmol sample of BING-5 product was placed in a beaker, followed by 1.5 mmol of potassium dichromate (Baker) and 50 mL of distilled water. Only the dichromate dissolved, yielding a yellow solution with BING-5 material on the bottom of the beaker. The beaker was covered with Parafilm and stirred mechanically at room temperature for the desired time. UV–vis was then performed by diluting 1.0 mL of solution to 50.0 mL with distilled water.



**Figure 4.** The series of UV–vis patterns of the anion-exchange solution shows that dichromate is gradually being absorbed (arrows) by BING-5, as corroborated by PXRD, <sup>14</sup>N NMR, and TGA.

Single crystals, however, retained their structure, while still uptaking dichromate in high capacity: we follow the uptake of dichromate by UV–vis of the exchange solution (Figure 4).<sup>36</sup> 12.7%, 46.3% and 52.0% of the dichromate from the original 0.030 M solution (added in 50% molar excess with respect to the BING-5 solid<sup>35</sup>) is absorbed after 0.5, 3, and 7 days, respectively.<sup>37</sup> This trend is corroborated by the following: (i) <sup>14</sup>N NMR of the exchange solution showed that nitrate was gradually being released into solution. A calculation based on <sup>14</sup>N peak areas relative to a known standard shows our material is 13.3%, 61.0%, and 86.0% exchanged after 0.5, 3, and 7 days, respectively.<sup>38</sup> (ii) When another lead-based material, such as PbO, was used in place of BING-5 as an exchange solid, no dichromate sorption occurred. The dichromate concentration was identical before and after 3 days of stirring, as judged by UV–vis spectroscopy. Similarly, the PXRD pattern of the PbO solid was unchanged.

(36) Relative absorbances were measured using the 450 nm peak of dichromate, at acceptable values of absorbance and away from any nitrate bands. It should also be noted that dichromate is being absorbed. No peaks of monochromate were seen, comparing to the UV–vis spectrum of a 0.03 M solution of K<sub>2</sub>CrO<sub>4</sub> (Baker). Dichromate solutions are also known to be highly stable (Harris, D. C., *Quantitative Chemical Analysis*, 4th ed.; W. H. Freeman: New York, 1995; p 439).

(37) While a small amount of PbCrO<sub>4</sub> does form after 7 days, the PXRD peak intensities are too low to account for these exchange percentages.

The ion-exchanged material (3 days, PXRD, Figure 2b) was placed in a 0.03 M HNO<sub>3</sub> solution, to see if the exchange could be reversed, replacing dichromate with nitrate. The analogous conditions of ion-exchange were used.<sup>35</sup> No reaction occurred after 3 days, as the ion-exchange solution was colorless, and only the one peak of nitrate (centered at 301 nm) was observed in a UV–vis spectrum. Presumably, the large hydration enthalpy of nitrate makes its re-intercalation highly unlikely, and is responsible for the selectivity of BING-5 for dichromate. We are therefore currently studying the intercalation of other inorganic and organic anions into our structure.

## Conclusions

BING-5 expands the known structure types of cationic materials beyond the isostructural set of LDHs. The structure represents our first efforts toward constructing cationic extended materials built from late group 14 elements. We are currently exploring other possible anionic structure-directing agents, such as transition metal complexes, organic anions, and carbonate. This report also shows an initial example of anion-exchange, and it is anticipated that other anion intercalation chemistry is possible with this material. Materials synthesis with anionic SDAs is a largely unexplored strategy, and it is highly plausible that a wide range of cationic inorganic materials await discovery, with potentially unique properties.

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**Supporting Information Available:** Crystallographic CIF file, containing refinement parameters, fractional atomic coordinates, bond lengths and bond angles. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(38) A TGA trace of the 3 day ion-exchanged solid (PXRD, Figure 2b) contained transitions identical with the as-synthesized solid, but only ca. 2.8 wt % was lost over the first thermal event, versus ca. 8.0 wt % (Figure 3). This reduced weight loss of ca. 65% agrees well with the <sup>14</sup>N NMR data. Dichromate would not volatilize off in the TGA, so both methods indicate the degree of anion-exchange.