Hydrogen adsorption in dehydrated variants of the cyano-bridged framework compounds $A_2Zn_3[Fe(CN)_6]_2 \cdot xH_2O$ (A = H, Li, Na, K, Rb)†

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The impact of coordinatively-unsaturated alkali-metal ions on hydrogen adsorption is studied in dehydrated variants of the compounds $A_2Zn_3[Fe(CN)_6]_2 \cdot xH_2O$ (A = H, Li, Na, K, Rb), revealing maximum adsorption enthalpies that vary from 7.7 kJ mol^{-1} for A = Na to 9.0 kJ mol^{-1} for A = K.

Owing to its clean oxidation, high energy density, and ability to be generated from a variety of energy sources, molecular hydrogen is currently being considered as a replacement for fossil fuels in mobile applications.[1] To accomplish this, however, an effective means of on-board storage must be developed. Recently, microporous coordination solids with high surface areas have emerged as promising hydrogen storage materials.[2] These compounds can show high H_2 uptake, but typically exhibit low H_2 adsorption enthalpies of 4–7 kJ mol^{-1}. Since a binding enthalpy of *ca.* 15 kJ mol^{-1} is expected to maximize reversible H_2 uptake at 298 K,[3] significantly higher adsorption enthalpies are needed in order to avoid the use of expensive and heavy cooling equipment. A promising strategy for increasing the adsorption enthalpy is to incorporate coordinatively-unsaturated metal centers capable of supporting strong metal–H_2 interactions within a porous solid.[4] This approach has already led to substantial enhancement in hydrogen adsorption enthalpy;[5] for example, generation of coordinatively-unsaturated Mn^{2+} sites in the metal–organic framework $Mn_3[(Mn_4Cl)_3(BTT)_8(CH_3OH)_{10}]_2$ (BTT^{3-} = 1,3,5-benzentristetrazolate) increased the zero-coverage H_2 adsorption enthalpy from 7.6 to 10.1 kJ mol^{-1}.[5c]

Previously, we[4a] and others[6] reported hydrogen storage in cyano-bridged coordination solids, specifically Prussian blue analogues of the type $M_3[Co(CN)_6]_2$. These cubic framework compounds contain coordinatively-unsaturated metal centers, which in the case of $Cu_3[Co(CN)_6]_2$ have been shown to interact with H_2 at high loading.[7] Unfortunately, however, the metal–H_2 interactions in the Prussian blue analogues characterized thus far are only of comparable strength to the van der Waals interactions between H_2 and the pore walls.[8] Here, we report the hydrogen storage properties for a series of dehydrated zinc-ferrocyanide compounds, wherein guest alkali-metal cations provide higher-energy H_2 adsorption sites.

Compounds of the type $A_2Zn_3[Fe(CN)_6]_2 \cdot xH_2O$ exhibit structures in which octahedral $[Fe(CN)_6]^{4-}$ complexes are linked *via* tetrahedrally-coordinated, N-bound Zn^{2+} ions to form a porous three-dimensional framework.[9] The anionic zinc-ferrocyanide framework is characterized by cages of the type depicted in Fig. 1, where each cage contains two guest alkali metal cations and 5–10 solvating water molecules. These water molecules can be removed upon heating under reduced pressure, leaving the zinc-ferrocyanide framework intact and generating open coordination sites on the guest cations. Thus, hydrogen can be expected to interact with the polarizable π-electron clouds of the cyanide bridges within the framework, and, more interestingly, directly with the guest cations.

To assess the impact of various exposed alkali-metal cations on H_2 binding, we investigated the hydrogen adsorption properties of the materials $A_2Zn_3[Fe(CN)_6]_2 \cdot xH_2O$ (A = H, Li, Na, K, Rb) upon dehydration. With the exception of A = Rb, the hydrated form of each compound was synthesized by reacting the corresponding $A_4[Fe(CN)_6]$ salt with $Zn(NO_3)_2 \cdot 6H_2O$ in aqueous solution.‡ The rubidium-containing compound was instead prepared by soaking $Na_2Zn_3[Fe(CN)_6]_2 \cdot 9H_2O$ in an aqueous solution of RbCl. Similar ion-exchange experiments with divalent and trivalent cations, such as Mg^{2+} and Al^{3+}, resulted in the partial decomposition of the framework to Prussian blue ($Fe_4[Fe(CN)_6]_3 \cdot 14H_2O$) and other insoluble metal-cyanide solids. The X-ray powder diffraction patterns of all five products were consistent with the usual $A_2Zn_3[Fe(CN)_6]_2$ structure type.[9] Elemental analysis confirmed the composition of each material and indicated the presence of less than 0.1 equivalents of any other alkali-metal ion. For A = Na, K and Rb, the solids were completely dehydrated by heating at 95 °C for 24 h

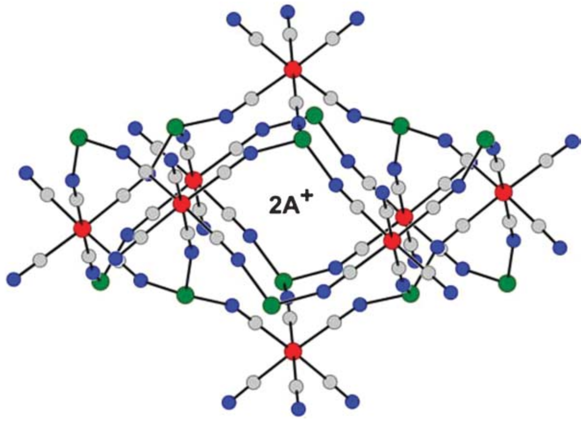

Fig. 1 Structure of a cage unit within the zinc-ferrocyanide frameworks of compounds of the type $A_2Zn_3[Fe(CN)_6]_2 \cdot xH_2O$. Green, red, grey, and blue spheres represent Zn, Fe, C and N atoms, respectively. Water solvate molecules and interstitial cations are omitted for clarity.

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under dynamic vacuum. For A = H and Li, complete dehydration of the material led to decomposition, as evidenced by broadening of the peaks in the X-ray diffraction pattern and the formation of Prussian blue. This decomposition is likely due to reaction of the A^+ cation with the anionic framework walls since H^+ and Li^+ are considerably stronger acids than Na^+, K^+ or Rb^+. In contrast, heating $H_2Zn_3[Fe(CN)_6]_2{\cdot}10H_2O$ or $Li_2Zn_3[Fe(CN)_6]_2{\cdot}10H_2O$ at 40 °C under reduced pressure for 48 h produced the crystalline phases $H_2Zn_3[Fe(CN)_6]_2{\cdot}2H_2O$ and $Li_2Zn_3[Fe(CN)_6]_2{\cdot}2H_2O$. Here, the remaining water molecules are likely coordinated to the guest H^+ and Li^+ ions, reducing their acidity. These partially dehydrated materials are only moderately stable, showing substantial decomposition to Prussian blue and other metal-cyanide extended solids after several weeks at room temperature under inert atmosphere.

The porosity of the dehydrated samples was probed *via* argon adsorption measurements performed at 87 K. With the exception of $H_2Zn_3[Fe(CN)_6]_2{\cdot}2H_2O$, all materials showed type I adsorption isotherms, characteristic of microporous materials (see Fig. S16–S20 in ESI†). The surface areas, calculated using the BET equation, are listed in Table 1 and range from 250 $m^2\ g^{-1}$ for $Li_2Zn_3[Fe(CN)_6]_2{\cdot}2H_2O$ to 570 $m^2\ g^{-1}$ for $Na_2Zn_3[Fe(CN)_6]_2$. The variations observed are likely due to differences in the size of the alkali-metal cations in the pores of the structures. It should be noted that the Ar adsorption capacity of 6.4 mmol g^{-1} measured for $K_2Zn_3[Fe(CN)_6]_2$ at 600 Torr compares well with the N_2 adsorption capacity of 6.1 mmol g^{-1} at 600 Torr and 77 K obtained previously for this material.[10] Significantly, owing to the differences in framework structure and the presence of guest cations, the surface areas observed for these zinc-ferrocyanide compounds are generally lower than those obtained for vacancy-riddled Prussian blue analogues of the type $M_3[Co(CN)_6]_2$.

In the case of $H_2Zn_3[Fe(CN)_6]_2{\cdot}2H_2O$, a type II adsorption isotherm was observed, with *ca.* 1 mmol Ar g^{-1} adsorbed at 600 Torr and a calculated BET surface area of just 40 $m^2\ g^{-1}$. Both O_2 and N_2 adsorption isotherms showed similarly low gas uptake capacities. A fit of the adsorption data to the Horvath–Kawazoe model[11] indicates that the observed gas adsorption is taking place primarily in void space with a diameter greater than 30 Å. In contrast, as seen in Fig. 2, the H_2 adsorption isotherms showed significant gas uptake (comparable to that observed for other $A_2Zn_3[Fe(CN)_6]_2$ compounds), indicating that the low uptake of Ar, O_2 and N_2 is due to the inability of these gases to enter the pores of the material, rather than a small pore volume. This behaviour is similar to the molecular sieving effect observed for $Mg_3(NDC)_3$ (NDC^{2-} = 2,6-naphthalenedicarboxylate), which adsorbs H_2 and O_2, but not N_2.[12] Based on this selective gas uptake, it can be inferred that the diameter of the pore openings in $H_2Zn_3[Fe(CN)_6]_2{\cdot}2H_2O$ is between 2.9 and 3.4 Å, the respective kinetic diameters of H_2 and Ar.[2f,13]

Table 1 Adsorption properties of dehydrated zinc-ferrocyanide compounds and the Prussian blue analogue $Zn_3[Co(CN)_6]_2$

Compound	SA[a]/ $m^2\ g^{-1}$	Wt% H_2[b]	g H_2 L^{-1}[b,c]	ΔH_{ads}[d]/ kJ mol^{-1}
$H_2Zn_3[Fe(CN)_6]_2{\cdot}2H_2O$		1.1	16	7.8–8.2
$Li_2Zn_3[Fe(CN)_6]_2{\cdot}2H_2O$	250	1.1	16	6.1–7.9
$Na_2Zn_3[Fe(CN)_6]_2$	570	1.2	18	7.0–7.7
$K_2Zn_3[Fe(CN)_6]_2$	470	1.2	19	7.9–9.0
$Rb_2Zn_3[Fe(CN)_6]_2$	430	1.1	19	7.3–7.9
$Zn_3[Co(CN)_6]_2$[4a]	720	1.4	18	6.3–6.5

[a] Surface area calculated using the BET model. [b] Measured at 77 K and 890 Torr. [c] Calculated assuming no reduction in unit cell volume upon dehydration. [d] Determined using the method described in the ESI.

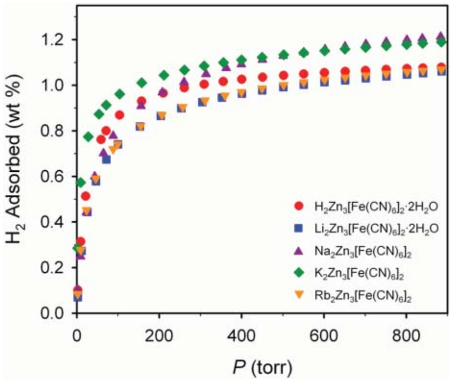

Fig. 2 Hydrogen adsorption isotherms for dehydrated forms of the compounds $A_2Zn_3[Fe(CN)_6]_2{\cdot}xH_2O$ (A = H, Li, Na, K, Rb).

Hydrogen adsorption isotherms were measured at 77 K for the five zinc-ferrocyanide compounds (see Fig. 2). In each case, the observed H_2 uptake was found to be fully reversible. Table 1 lists the storage capacities at the maximum attainable pressure of 890 Torr. Note that the values vary slightly according to the size of the guest cation. The compounds containing the smaller Na^+ and K^+ ions store *ca.* 1.2 wt% H_2, while those containing the larger H_3O^+, $Li(H_2O)^+$ and Rb^+ ions store *ca.* 1.1 wt% H_2. Assuming only negligible reductions in unit cell volumes as a result of dehydration, this gives minimum volumetric H_2 storage densities in the range 16–19 g L^{-1} at 890 Torr. These densities lie in the same range as those determined for the cubic Prussian blue analogues $M_3[Co(CN)_6]_2$ (M = Mn, Fe, Co, Ni, Zn), but are lower than the density of 25 g L^{-1} observed for $Cu_3[Co(CN)_6]_2$.[4a] Most significantly, compared with the results obtained previously for Prussian blue analogues, the hydrogen adsorption isotherms of the zinc-ferrocyanide materials exhibit a steeper initial rise and appear closer to saturation at 890 Torr, signalling a stronger interaction between H_2 and the framework.

In order to quantify the strength of this interaction, a second hydrogen isotherm was measured for each compound at 87 K. Taking both the 77 and 87 K data, the enthalpy of adsorption as a function of hydrogen uptake was then calculated using a variant of the Clausius–Clapeyron equation.[11] The results, plotted in Fig. 3, show maximal enthalpies ranging from 7.7 kJ mol^{-1} for A = Na to 9.0 kJ mol^{-1} for A = K, and represent the highest values yet observed for cyano-bridged compounds.[4a,8,14] As expected, significant changes occur as the cation A^+ is varied. However, since the trends in unit cell dimensions and, therefore, framework pore sizes do not correlate with the trend in enthalpy of adsorption,[9] the observed trend of $K^+ > (H_3O)^+ > Rb^+ \approx Li(H_2O)^+ > Na^+$ must be predominantly due to interactions between hydrogen and the guest cations. Interestingly, this result differs substantially from the expected inverse correlation with ionic radius, which is in line with experimental observations in the gas phase.[15] It also differs from the trend of $Li^+ > Na^+ > K^+$ observed for hydrogen interacting with alkali-metal cations in LSX-type zeolites.[16] These discrepancies may be due to the relatively small pore size of the $A_2Zn_3[Fe(CN)_6]_2$ frameworks, which might enable small cations to burrow into crevices within the negatively-charged cyano-bridged framework

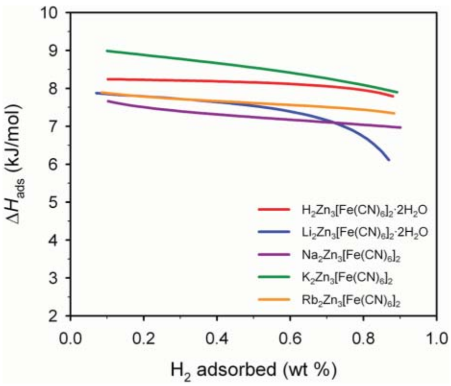

Fig. 3 Adsorption enthalpies for dehydrated forms of the compounds $A_2Zn_3[Fe(CN)_6]_2 \cdot xH_2O$ (A = H, Li, Na, K, Rb).

surface, thereby mitigating their polarizing power. In turn, it may also facilitate simultaneous interactions of bound H_2 molecules with the pore walls, thereby raising the binding enthalpies for materials containing larger cations. Note that a loading of one H_2 molecule per A^+ cation occurs between 0.51 and 0.61 wt% for these compounds. Thus, the sudden downturn in ΔH_{ads} observed for $Li_2Zn_3[Fe(CN)_6]_2 \cdot 2H_2O$ at loadings above 0.6 wt% suggests that each $Li(H_2O)^+$ moiety can bind just one H_2 molecule, whereas the other guest cations can apparently each bind more than one.

The foregoing results demonstrate the utility of guest alkali-metal cations for enhancing the H_2 binding affinity within microporous coordination solids. Future work on these materials will include the use of neutron diffraction methods in studying the metal–H_2 interactions, as well as attempts to incorporate other monovalent guest cations, such as Cu^+,[17] expected to exhibit higher H_2 binding enthalpies and further increase the temperature at which hydrogen can be stored.

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Notes and references

‡ The compounds $H_4[Fe(CN)_6]$, $Na_2Zn_3[Fe(CN)_6]_2 \cdot 9H_2O$ and $K_2Zn_3[Fe(CN)_6]_2 \cdot 9H_2O$ were synthesized according to published procedures.[18,19] Water was distilled and deionized with a Milli-Q filtering system. All other reagents were obtained from commercial sources and used without further purification. The powder X-ray diffraction pattern of each product was observed to match the pattern simulated from the crystal structure of $K_2Zn_3[Fe(CN)_6]_2 \cdot 9H_2O$.[9a]

Synthesis of $H_2Zn_3[Fe(CN)_6]_2 \cdot 10H_2O$: A solution of $Zn(NO_3)_2 \cdot 6H_2O$ (1.5 g, 5.0 mmol) in 10 mL of water was added dropwise to a stirred solution of freshly-prepared $H_4[Fe(CN)_6]$ (0.71 g, 3.3 mmol) in 6.7 mL of water. The resulting white precipitate was allowed to sit in the mother-liquor for 1 h, and was then collected by filtration, washed with successive aliquots of water (5 × 50 mL), and dried in air to give 1.2 g (82%) of product. Anal. Calc. for $C_{12}H_{22}Fe_2N_{12}O_{10}Zn_3$: C, 16.79; H, 2.58; Fe, 19.52; N, 19.59; Zn, 22.86. Found: C, 16.82; H, 2.63; Fe, 19.34; N, 19.13; Zn, 22.98%.

Synthesis of $Li_2Zn_3[Fe(CN)_6]_2 \cdot 10H_2O$: A freshly-prepared sample of $H_4[Fe(CN)_6]$ (0.71 g, 3.3 mmol) was dissolved in 6.7 mL of water. The resulting solution was quickly titrated to pH = 7 using 5 M $LiOH_{(aq)}$ to give an aqueous solution of $Li_4[Fe(CN)_6]$. A solution of $Zn(NO_3)_2 \cdot 6H_2O$ (1.5 g, 5.0 mmol) in 10 mL of water was then added dropwise to the stirred solution of $Li_4[Fe(CN)_6$. The resulting white precipitate was allowed to sit in the mother-liquor for 1 h, and was then collected by filtration, washed with successive aliquots of water (5 × 50 mL), and dried in air to give 1.0 g (71%, based on $H_4[Fe(CN)_6]$) of product. Anal. Calc. for $C_{12}H_{20}Fe_2Li_2N_{12}O_{10}Zn_3$: C, 16.56; H, 2.32; Fe, 19.26; Li, 1.59; N, 19.32; Zn, 22.55. Found: C, 16.44; H, 2.51; Fe, 18.89; Li, 1.73; N, 19.02; Zn, 22.12%.

Synthesis of $Rb_2Zn_3[Fe(CN)_6]_2 \cdot 5H_2O$: A sample of $Na_2Zn_3[Fe(CN)_6]_2 \cdot 9H_2O$ (1.0 g, 1.1 mmol) was immersed in 20 mL of a saturated aqueous solution of RbCl. After 24 h, the reaction mixture was filtered and the solid was immersed in 20 mL of a saturated aqueous solution of RbCl. This process was repeated five times, and the resulting white solid was dried in air to give the ion-exchanged product in quantitative yield. Anal. Calc. for $C_{12}H_{10}Fe_2N_{12}O_5Rb_2Zn_3$: C, 15.37; H, 1.07; Fe, 17.88; N, 17.94; Na, 0.00; Rb, 18.24; Zn, 20.93. Found: C, 15.24; H, 1.33; Fe, 18.06; N, 17.66; Na, <0.1; Rb, 18.05; Zn, 20.97%.

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