Coordination Polymers

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A Simple Lithium(I) Salt with a Microporous Structure and Its Gas Sorption Properties**

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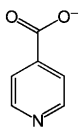
Much effort has been invested in studying the gas sorption properties of various classes of microporous materials such as zeolites,[1] activated carbon materials,[2] carbon nanotubes,[3] polymers of intrinsic microporosity,[4] and coordination polymers.[5] At a time in the early 1990s when few coordination polymers had been deliberately constructed and characterized, their ability to sorb gases was a reasonable expectation. The first experimental measurements that heralded great promise of coordination polymers as materials for useful gas storage were reported by Kitagawa and co-workers in 1997.[6] Subsequently, gas sorption by coordination polymers (more recently rebranded metal–organic frameworks (MOFs) by some) has become an intensively studied area.[5] Low density is a most desirable characteristic of any gas storage material intended for mobile applications, and materials based on "light" metals (such as Li, Mg, and Al) are obvious targets for exploration.[7,8] We report herein the synthesis, structure(s), and sorption properties of a simple salt of Li^+, lithium isonicotinate, which has a microporous structure and shows reversible gas uptake and release.

Well-formed crystals of composition $[(Li^+)(C_6H_4NO_2^-)]\cdot 0.5DMF$ (where $C_6H_4NO_2^-$ is the isonicotinate anion, **1**) can be readily obtained from DMF solution.[9] The structure, which was determined by single-crystal X-ray diffraction, consists of a 3D $[(Li^+)(C_6H_4NO_2^-)]$ network that contains microchannels occupied by DMF molecules.[10] All the isonicotinate units are equivalent, and are associated with four Li^+ centers, which are also all equivalent, and each associates with four isonicotinate anions. The structure can be readily envisaged in terms of $[(Li^+)(C_6H_4NO_2^-)]$ chains (see Figure 1a), that are linked together by Li^+–N interactions into 2D sheets (see Figure 1b). The sheets in turn are linked together by Li^+–N interactions to form the 3D network (see Figure 1c). As can be seen in Figure 1a, each chain consists of alternating four-membered rings (LiOLiO) and eight-membered rings (LiOCOLiOCO). The N centers of half of the pyridine units that



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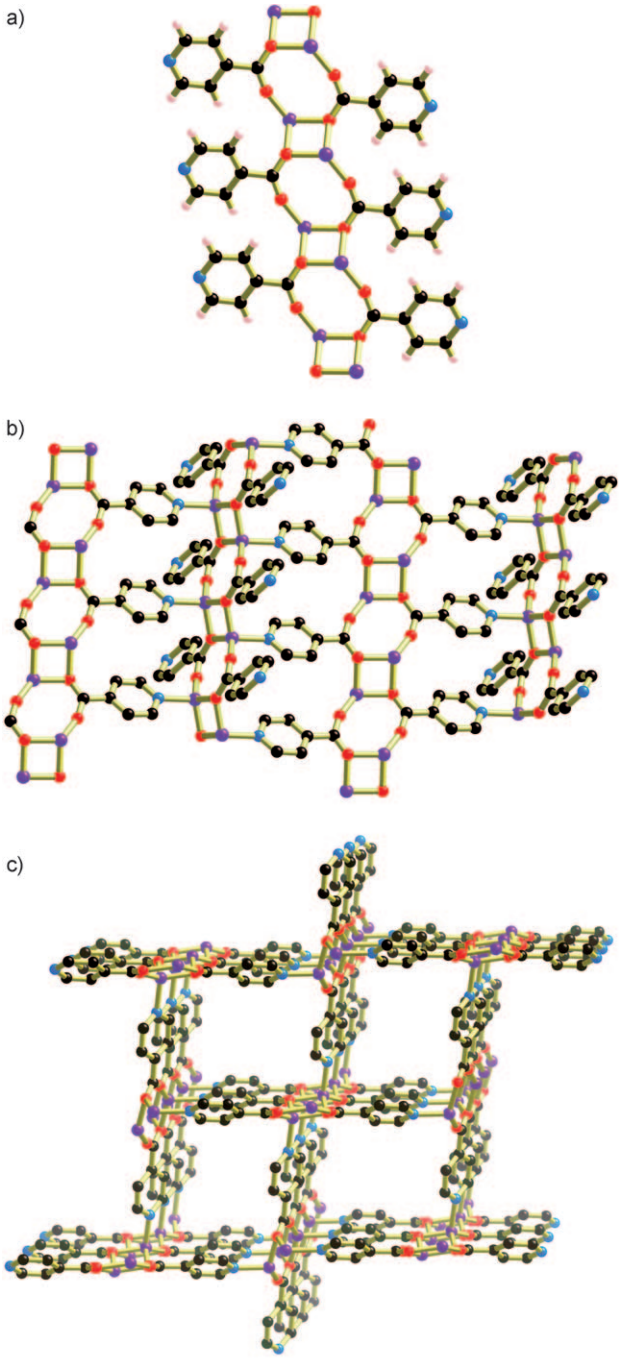

Figure 1. The structure of $[Li^+(C_6H_4NO_2^-)]\cdot 0.5\,DMF$. a) $[Li^+(C_6H_4NO_2^-)]$ chains. b) The association of chains to form sheets. c) The association of sheets to form the 3D framework, seen here looking down the channels. C black, O red, N blue, Li purple. Equivalent sheets of the type shown in (b) can be seen here in roughly the horizontal and vertical planes. Hydrogen atoms have been omitted for clarity.

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project out from the chain seen in Figure 1a interact with the Li^+ centers of the two adjacent chains to form the sheet. The remaining pyridine units (those not involved in the formation of the sheets) interact with the Li^+ centers in adjacent sheets to generate the 3D network seen in Figure 1c. Sheets such as that in Figure 1b can in fact be discerned in two distinct planes inclined to each other; any particular chain is shared by two equivalent sheets, as can be seen in Figure 1c. Disordered DMF molecules, which were modeled over four orientations, occupy the channels. The DMF can be removed from the channels to generate a material that sorbs gases as described below.

Procedures similar to that used to obtain the DMF solvated compound afford crystals of compositions $[(Li^+)(C_6H_4NO_2^-)]\cdot 0.5\,C_5H_9NO$ (C_5H_9NO = *N*-methylpyrrolidinone) and $[(Li^+)(C_6H_4NO_2^-)]\cdot 0.5\,C_4H_9NO$ (C_4H_9NO = morpholine) in a form suitable for X-ray diffraction studies. Although the morpholine and *N*-methylpyrrolidinone solvates crystallize in space groups that are different to that of the DMF solvate (see the Supporting Information), the same network topology is seen in all three; however there are some minor differences in geometry. The morpholine and *N*-methylpyrrolidinone molecules are located in the channels. While the morpholine is disordered, the *N*-methylpyrrolidinone is ordered.

All three compounds exhibit high thermal stability upon desolvation. Thermogravimetric analysis of the DMF solvate indicate that solvent loss (calcd 22.1%, found 21.1%) occurs in the range 25–141 °C. No further mass loss is apparent until approximately 370 °C, whereupon decomposition occurs. Similar TGA traces are found with the morpholine (calcd 25.2, found 24.9%) and *N*-methylpyrrolidinone (calcd 27.8, found 27.6%) solvates. Details of the thermogravimetric analysis are presented in the Supporting Information.

The dimensions of the approximately rectangular channels, defined by the van der Waals surfaces of the framework atoms are approximately 4×5.5 Å. Following removal of DMF under vacuum at a temperature of 110 °C, the ability of the residue to sorb hydrogen was examined at 77 K using a volumetric method. The isotherm for this sorption process, which is presented in Figure 2, shows an increase in the amount of hydrogen sorbed as the pressure is increased to approximately 640 kPa, when the H_2 uptake is 86 mL H_2 (at standard temperature and pressure, STP) per gram of compound. This uptake corresponds to two H_2 molecules per unit cell—the same guest/host ratio as present in the solvated compound. This result is consistent with the reasonable expectation from the crystallographic analysis that at least one hydrogen molecule will occupy the space vacated by a single solvent molecule. As the pressure is increased further, a slight dip is apparent in the isotherm. This is a commonly observed phenomenon with high pressure measurements, and arises from the fact that the measurement indicates the surface excess, a value that is an underestimate of the total sorption.[11] The desorption isotherm follows a similar return path; however some hysteresis is apparent. The isosteric heat of H_2 sorption was calculated by fitting a virial-type thermal adsorption equation to the 77 K and 87 K surface excess sorption data. The results indicate a relatively high value of 9.9 kJ mol^{-1} at zero loading. This value drops to 8.9 kJ mol^{-1} at 50% loading and finally to 6.5 kJ mol^{-1} at close to the maximum loading achieved. Coordination networks (or MOFs) that exhibit hydrogen sorption typically have heat of sorption values in the range 5–7 kJ mol^{-1}, and a small number have values that exceed 9 kJ mol^{-1}.[12–14] Champness, Schröder, and co-workers recently reported two coordination polymers that exhibit heat of adsorption values for H_2 of 9.0 and 10.1 kJ mol^{-1}.[15] The higher of the two values was attributed to a Li–H_2 interaction that involves an "exposed" Li^+ ion; the other compound contained no lithium. The Li^+ ion of lithium isonicotinate is surrounded roughly tetrahedrally by one nitrogen and three oxygen centers and therefore appears inaccessible to H_2; it does seem unlikely that the relatively high value of 9.9 kJ mol^{-1} we observe is due to some direct interaction between Li^+ and H_2. High values for heat of adsorption have been attributed previously to small pore sizes and our relatively high value may have a similar origin.[12,15,16] An H_2 binding energy in the range 15–20 kJ mol^{-1} is commonly recognized as desirable for useful room-temperature hydrogen storage.[13,14,17] Whilst our value falls short of this ideal, our results provide considerable encouragement that compounds of this type may prove useful.

The sorption of nitrogen, methane, and carbon dioxide was also investigated. The sorption results for all gases are presented in Table 1. The Brunauer–Emmett–Teller (BET) surface area determined on the basis of N_2 sorption at 77 K is 190 m^2 g^{-1}. The sorption and desorption isotherms are presented in the Supporting Information. Significant hysteresis was apparent for hydrogen and nitrogen sorption at 77 K. We

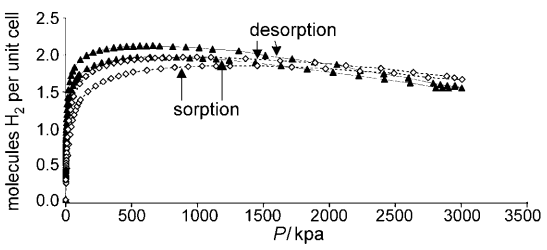

Figure 2. Isotherms for hydrogen sorption at 77 (▲) and 87 K (◇). The isotherms show the surface excess, not the absolute amount of H_2 sorbed.

Table 1: Gas sorption studies of lithium isonicotinate.

Gas	*T* [K]	Amount sorbed [mL (STP) g^{-1}]/molecules per unit cell	Pressure [kPa]	Heat of sorption (at zero loading) [kJ mol^{-1}]
H_2	77	85.6/1.97	641.3	9.9
	87	80.3/1.86	1141	
N_2	77	60.9/1.40	98.6	18.8
	87	53.2/1.22	200.3	
CO_2	258	82.6/1.69	2163	34.9
	273.2	74.1/1.51	3016	
	298.2	64.8/1.24	2775	
CH_4	258	62.0/1.37	3040	17.7
	273.2	58.1/1.26	3040	
	298.2	48.7/0.99	3047	

can only speculate as to the origin of the hysteresis, but it may be a consequence of the narrow channels that lead to sluggish diffusion of the sorbed gas molecules. Such explanations have been offered to explain hysteresis in other coordination networks.[18]

In conclusion, we have described the first example of a simple lithium salt with a microporous structure capable of hysteretic reversible sorption of a number of gases. The results provide proof-of-concept that simple salts of lightweight cations together with appropriately chosen organic anions are capable of reversible gas sorption. Whilst lithium isonicotinate shows only modest gas-sorbing capacities, the gas binding energies are encouragingly high. It would be worthwhile to explore templates larger than the DMF, morpholine, and *N*-methylpyrrolidinone used here, which may generate $[(Li^+)(C_6H_4NO_2^-)]$ frameworks of different topologies with larger channels. Moreover, many potentially effective anions other than the isonicotinate ion used here can be readily envisaged. We anticipate that the system described here may be the first example of a new class of microporous, gas-sorbing Li^+ salts.

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[9] Preparation of $[(Li^+)(C_6H_4NO_2^-)]$ solvate: The general procedure is illustrated here with the example of $[(Li^+)(C_6H_4NO_2^-)]\cdot 0.51$ DMF. Isonicotinic acid (1.680 g) and $LiOH\cdot H_2O$ (0.573 g) were dissolved in boiling methanol (15 mL). Dimethylformamide (40 mL) was added and the mixture was evaporated whilst the vapor temperature was monitored. When the vapor temperature reached 145 °C, the clear solution was allowed to cool, and deposited well-formed colorless crystals that were collected, washed with a little DMF, and dried briefly in vacuum. Yield: 1.97 g (87 %). Analysis of compound following removal of DMF under vacuum at a temperature of 110 °C for two hours. Elemental analysis calcd (%) for $LiC_6H_4NO_2\cdot 0.25\,H_2O$: C 53.96, H 3.40, N 10.49 %; found: C 53.88, H 3.31, N 10.50 %.
[10] Crystal data for $[Li(C_6H_4NO_2)_2]\cdot$DMF $M_r = 331.08$, monoclinic, $P2_1/n$, $a = 5.40280(10)$, $b = 13.9175(2)$, $c = 11.2862(3)$ Å, $\beta = 102.875(2)°$, $V = 827.31(3)$ Å^3, $Z = 2$, $\theta_{max} = 73.1°$, $Cu_{K\alpha}$ radiation $\lambda = 1.54184$ Å, $T = 130$ K, $\mu(Cu_{K\alpha}) = 0.824$ mm^{-1}, 3933 reflections measured, 1616 unique which were used in all calculations, 117 parameters. The structure was solved by direct methods and refined using a full-matrix least squares procedure (SHELX97),[19] $wR2 = 2151$ (all data) and $R1 = 0.0649$ ($I > 2\sigma(I)$). Crystallographic analysis was performed using the winGX system of programs.[20] Crystal data for $[Li(C_6H_4NO_2)_2]\cdot$morpholine $M_r = 345.21$, triclinic, $P\bar{1}$, $a = 5.3968(3)$, $b = 11.4886(9)$, $c = 13.4233(9)$ Å, $\alpha = 90.670(6)$, $\beta = 94.900(5)$, $\gamma = 91.238(6)°$, $V = 828.96(10)$ Å^3, $Z = 2$, $\theta_{max} = 67.99$, $Cu_{K\alpha}$ radiation $\lambda = 1.54184$ Å, $T = 130$ K, $\mu(Cu_{K\alpha}) = 0.844$ mm^{-1}, 5040 reflections measured, 3017 unique which were used in all calculations, 270 parameters. The structure was solved by direct methods and refined using a full-matrix least squares procedure (SHELX97),[19] $wR2 = 0.2267$ (all data) and $R1 = 0.0838$ ($I > 2\sigma(I)$). Crystallographic analysis was performed using the winGX system of programs.[20] Crystal data for $[Li(C_6H_4NO_2)_2]\cdot N$-methylpyrrolidinone $M_r = 357.22$, monoclinic, $P2_1$, $a = 5.47330(10)$, $b = 13.4580(2)$, $c = 11.7304(2)$ Å, $\beta = 101.166(2)°$, $V = 847.70(2)$ Å^3, $Z = 2$, $\theta_{max} = 73.35$, $Cu_{K\alpha}$ radiation $\lambda = 1.54184$ Å, $T = 130$ K, $\mu(Cu_{K\alpha}) = 0.847$ mm^{-1}, 4084 reflections measured, 1760 unique which were used in all calculations, 245 parameters. The structure was solved by direct methods and refined using a full-matrix least squares procedure (SHELX97),[19] $wR2 = 0.1032$ (all data) and $R1 = 0.0393$ ($I > 2\sigma(I)$). Crystallographic analysis was performed using the winGX system of programs.[20] CCDC 753374 ($[Li(C_6H_4NO_2)_2]\cdot$morpholine), 753375 ($[Li(C_6H_4NO_2)_2]\cdot$DMF), and 753376 ($[Li(C_6H_4NO_2)_2]\cdot N$-methylpyrrolidinone) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
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