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Crystal and Molecular Studies of Succinimide-Lithium Salt Complexes

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We discovered a new class of succinimide–lithium complexes with highly symmetric tetrahedral geometry that can accommodate a variety of anions. Of the seven succinimide–lithium salt complexes prepared and examined by solution- and solid-state complexation methods, three crystal structures are reported. The present results show that lithium ions strongly coordinate carbonyls of succinimide molecules. In the crystal structures of (succinimide)$_2$LiNO$_3$ (**3**), (succinimide)$_2$LiI (**4**), and (succinimide)$_2$LiPF$_6$ (**7**), the lithium ion is tetrahedrally coordinated by four carbonyls of four succinimide molecules. The anion in each structure takes part in an ion–dipole interaction with the imide N–H hydrogen atom. Other lithium salts, such as LiBF$_4$, LiClO$_4$, LiBr, and LiCl, are crystallographically isomorphous to (succinimide)$_2$LiI and (succinimide)$_2$LiPF$_6$, differing slightly in the unit-cell dimensions. (Succinimide)$_2$LiNO$_3$, however, crystallizes in a lower symmetry group because the nitrate group is not spherelike but disk shaped. The X-ray crystal structures of three succinimide–lithium salt complexes [(succinimide)$_2$LiX, X = I$^-$, NO$_3^-$, PF$_6^-$] are examined to show how the molecular volumes and shapes of these anions affect lithium–imide complexation in the solid state.

Introduction

Ion–molecule interactions that compete with preformed hydrogen-bonded networks have important implications in biological systems. The effects of lithium salts in biological systems have been studied extensively due to their use in treating manic depression and other neurological disorders.[1] There has been much interest in coordination properties of Li$^+$ as they relate to its biological activity. Li$^+$, the smallest alkali metal cation (r = 0.6 Å),[2] is a hard Lewis acid which interacts with hard Lewis bases such as ethers,[3] amides,[4] carboxylates,[5] and phosphates.[6] Crystal structures of most Li$^+$ complexes in ion–dipole type interactions have revealed that they exhibit 4-fold tetrahedral or 5-fold square-pyramidal geometries.[7]

In our investigation of how ion–dipole interactions compete with preformed hydrogen-bonded networks, we have found that imide carbonyl groups act as hard bases that strongly interact with Li$^+$. In this paper, molecular complexes of succinimide and lithium salts are prepared and characterized in the solid state. We show that the surface areas and shapes of anions (Cl$^-$, Br$^-$, NO$_3^-$, I$^-$, BF$_4^-$, ClO$_4^-$, PF$_6^-$) are important factors that affect lithium–imide complexation in the solid state.

Experimental Section

General Methods. Infrared spectra were recorded on a Nicolet 510M FTIR spectrometer as Nujol mulls and are reported in cm^{-1}. X-ray powder diffraction patterns (XRD) were obtained on a Siemens D-500 diffractometer using Cu Kα radiation and a scintillation detector. Succinimide and lithium metal salts were purchased from Aldrich and used without further purification. In all cases, colorless pyramidal or bipyramidal crystals were obtained.

General Methods of Preparation. Succinimide$_2$(LiX), where X = Cl$^-$, Br$^-$, NO$_3^-$, I$^-$, BF$_4^-$, ClO$_4^-$, and PF$_6^-$, complexes are prepared by both solution and solid-state techniques.

Solution method: A 2:1 molar ratio of succinimide and LiX was dissolved in methanol or in a 1:1 acetonitrile–methanol mixture and allowed to recrystallize slowly at room temperature. Crystals were removed from solution before the solvent completely evaporated.

Solid-state method: A 2:1 molar ratio of succinimide and LiX was ground together in a SPEX 5100 mixer/mill for 10 min. Conversion of the starting materials to the (succinimide)$_2$LiX complex in the solid state was determined to be quantitative by the absence of starting material peaks in solid-state FTIR spectrum and X-ray powder diffraction pattern.

Succinimide$_2$(LiCl) (1): IR[8] 2770, 2738, 1794, 1746, 1690, 1410, 1302, 1258, 1205, 860 cm^{-1}; XRD $[d(I/I_0)]$ 11.15(8.58), 11.45(6.29), 12.15(81.11), 16.30(71.31), 18.2(21.62), 19.5(23.51), 22.80(17.88), 31.20(100.00), 31.45(40.17).

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[†] Deceased June 10, 1992.

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(1) (a) *Lithium-Current Applications in Science, Medicine, and Technology*; Bach, R. O., Ed.; Wiley-Interscience: New York, 1985. (b) Tosteson, D. *Sci. Am.* **1981,** *244,* 164–175. (c) Lazarus, J. H.; Collard, K. J. *Endocrine and Metabolic Effects of Lithium*; Plenum: New York, 1986.

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(5) (a) Enders-Beumer, A.; Harkema, S. *Acta Crystallogr. B* **1973,** *29,* 682–685. (b) Klapper, V. H.; Kuppers, H. *Acta Crystallogr. B* **1973,** *29,* 21–26. (c) Gabe, E. J.; Glusker, J. P.; Minkin, J. A.; Patterson, A. L. *Acta Crystallogr.* **1967,** *22,* 366–375. (d) Hinazumi, H.; Mitsui, T. *Acta Crystallogr. B* **1972,** *28,* 3299–3305.

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(8) No N–H absorbance was observed in the IR spectrum of the (succinimide)$_2$-LiCl complex. Nujol peaks around 3000 cm^{-1} may interfere with its detection, and attempts to use a KBr pellet were unsuccessful due to anion exchange with the complex.

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Succinimide$_2$(LiBr) (2): IR 3423, 3134, 3091, 3058, 1854, 1790, 1746, 1688, 1409, 1390, 1300, 1254, 1204, 1023, 929, 858, 826, 807 cm^{-1}; XRD [$d(I/I_0)$] 12.40(1.94), 18.70(100.00), 23.05(1.97), 25.00(2.98), 26.30(3.82), 29.55(2.10), 29.20(3.08), 32.70(2.05), 37.85(7.18).

Succinimide$_2$(LiNO$_3$) (3): IR 3428, 3123, 1792, 1748, 1696, 1420, 1327, 1298, 1207, 1157, 827 cm^{-1}; XRD [$d(I/I_0)$] 11.10(100.00), 15.95(10.42), 18.4(4.61), 19.10(4.19), 22.15(5.23), 28.9(3.51), 29.6(7.32), 30.40(3.39), 31.40(7.54).

Succinimide$_2$(LiI) (4): IR 3422, 3106, 3046, 2738, 1854, 1782, 1744, 1686, 1559, 1406, 1296, 1250, 1200, 1157, 925, 856, 825, 771 cm^{-1}; XRD [$d(I/I_0)$] 12.25(3.10), 18.15(100.00), 22.90(7.58), 25.45(5.42), 26.05(4.34), 29.10(5.23), 29.35(5.00), 31.90(5.21), 34.05(3.90).

Succinimide$_2$(LiBF$_4$) (5): IR 3435, 3316, 1788, 1750, 1694, 1421, 1410, 1395, 1299, 1252, 1206, 1063, 925, 860, 831 cm^{-1}; XRD [$d(I/I_0)$] 10.80(100.00), 13.35(2.70), 15.70(14.31), 17.45(1.98), 18.05(6.74), 18.80(5.87), 21.80(8.57), 22.00(5.23), 24.4(2.44), 28.40(3.71), 29.00(19.32), 29.95(7.43), 30.40(2.36), 31.50(28.04), 37.7(41.48).

Succinimide$_2$(LiClO$_4$) (6): IR 3281, 1786, 1748, 1690, 1419, 1408, 1392, 1298, 1251, 1203, 1095, 925, 859, 827, 724 cm^{-1}; XRD [$d(I/I_0)$] 10.70(100.00), 15.60(6.01), 17.90(5.12), 18.65(2.98), 21.65(4.32), 21.85(3.93), 24.2(2.62), 28.80(9.35), 31.4(12.29).

Succinimide$_2$(LiPF$_6$) (7): IR 3378, 3233, 1854, 1758, 1693, 1425, 1412, 1298, 1250, 1199, 855, 818, 719, 650 cm^{-1}; XRD [$d(I/I_0)$] 10.25(7.59), 10.55(72.37), 15.40(7.14), 28.50(5.01), 31.40(10.62), 37.60(100.00).

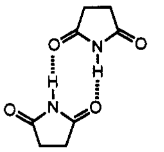
Metal salts that failed to form complexes: Several attempts have been unsuccessful in forming complexes using both solution and solid-state methods described in the experimental section. Using these conditions, succinimide does not form complexes with the following metal salts: LiF, Li_2CO_3, Li_2SO_4, Li_2IO_3, NaF, NaCl, NaBr, NaI, $NaPF_6$, KCl, KBr, KI, $MgBr_2$, $MgSO_4$, and $CaBr_2$.

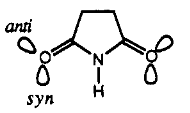
Crystallographic Literature Search. A connectivity search of the Cambridge Crystallographic Data Base (Version 5.0)[9] was performed for acyclic and cyclic imide/metal complexes for the C–CO–NH–CO–C imide fragment. All imide–metal salt crystal structures were diacetamide complexes with group I or II metal halides, and no cyclic imide and metal salt complexes were found.

Crystal Structure Determinations. Experimental details of the X-ray analyses of the three imide-metal salt complexes are listed in Table 1. Crystal structural data were collected on an Enraf-Nonius CAD-4 diffractometer with graphite monochromated, Mo Kα radiation (λ = 0.710 73) at 297 K. Lattice parameters were obtained from least-squares refinement using 24–25 centered reflections. All structures were corrected for Lorentz and polarization effects. Correction for secondary extinction was applied for each structure. Structures were solved by direct methods with MITHRIL[10] and DIRDIF.[11] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms included in the structure factor calculation were placed in idealized positions ($d_{C-H} = d_{N-H}$ = 0.95 Å).

Results

Succinimide molecules aggregate in dimers through NH···O bonds using the *syn* lone pairs of electrons of the imide carbonyl groups as shown below:[12]





Specific structural changes of the succinimide aggregates occur as a metal ion competes with the hydrogen bonds and becomes incorporated into the crystal structure. The complexation of succinimide with lithium metal salts was investigated to determine how cyclic imides interact with these ions. Of the seven (succinimide)$_2$LiX complexes prepared, we have characterized three of them by X-ray single-crystal structural analysis and obtained space-group and unit-cell dimensions for the other four structures in order to correlate their structural similarities. Selected intra- and intermolecular bond lengths and geometries of the three structures are given in Table 5.

Table 1. Crystallographic Data

compd	**3**	**4**	**7**
crystal size (mm^3)	0.6 × 0.6 × 0.5	0.5 × 0.5 × 0.5	0.49 × 0.45 × 0.35
emp formula	$C_8H_{10}N_3O_7Li$	$C_8H_{10}N_2O_4LiI$	$C_8H_{10}N_2O_4LiPF_6$
fw	267.12	332.02	350.08
space group	$P4_12_12$	$I4_1/amd$	$I4_1/amd$
$a = b$ (Å)	7.755 (3)	7.763 (3)	8.029 (3)
c (Å)	19.657 (6)	19.56 (1)	20.550 (5)
$\alpha = \beta = \gamma$ (deg)	90	90	90
Z	4	4	4
vol (Å^3)	1182 (1)	1179(2)	1325 (1)
d_{calc} (g/cm^3)	1.501	1.871	1.754
μ (Mo Kα)	1.23	26.83	2.89
scan technique	ω–2θ	ω–2θ	ω
2θ_{max} (deg)	59.9	59.9	59.8
scan speed (deg/min in ω)	16.5	16.5	2.1
measd unique reflns	1751	540	658
reflns used	1080	459	499
R^a (%)	0.073	0.043	0.048
$R_w{}^b$ (%)	0.086	0.059	0.065
range of h, k, l	$-10 \le h \le 10$ $0 \le k \le 10$ $0 \le l \le 27$	$0 \le h \le 9$ $0 \le k \le 10$ $-25 \le l \le 25$	$-10 \le h \le 11$ $-11 \le k \le 11$ $-26 \le l \le 28$
(shift/error)$_{max}$	0.00	0.00	0.01
final Δ electron density (e$^-$/Å^3)	0.3	1.13	0.37

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [(\sum w(|F_o| - |F_c|^2/\sum wF_o{}^2)]^{1/2}$; $w = 4F_o2/\sigma^2(F_o)^2$.

Table 2. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters (Å^2) of (Succinimide)$_2$LiNO$_3$ (3) with Esd's in Parentheses

atom	x	y	z	$B_{eq}{}^a$
O(1)	0.7666(3)	0.5538(2)	0.44566(9)	3.57(8)
O(2)	0.7638(3)	−0.0293(2)	0.4452(1)	4.05(9)
N	0.7681(3)	0.2630(2)	0.4316(1)	3.64(9)
C(1)	0.7617(4)	0.4073(3)	0.4697(1)	2.9(1)
C(2)	0.7428(5)	0.3574(3)	0.5430(1)	3.6(1)
C(3)	0.7544(5)	0.1616(3)	0.5429(1)	3.7(1)
C(4)	0.7601(4)	0.1131(3)	0.4695(1)	3.2(1)
Li$^+$	0.7666(5)	0.7666	$^1/_2$	3.1(1)
H	0.7772	0.2652	0.3834	4.0
H(S)	0.8435	0.4018	0.5678	4.1
H(S)	0.6438	0.3992	0.5630	4.1
H(S)	0.8464	0.1197	0.5677	4.3
H(S)	0.6470	0.1171	0.5619	4.3
O(3)	0.6212(4)	0.7524(7)	0.9565(2)	10.7(2)
O(4)	0.688(1)	0.843(1)	1.0340(7)	15.4(7)
O(5)	0.8350(8)	0.8350	1.00	19.5(7)
N(1)	0.7372(4)	0.7372	1.00	5.10(8)

[a] $B_{eq} = {}^1/_3\sum_i\sum_j B_{ij}a_i{}^*a_j{}^*a_ia_j$.

Crystal Properties. Crystalline adducts of succinimide and lithium metal salts were prepared by dissolving 2:1 stoichiometric amounts of the imide and the metal salt in 1:1 methanol/acetonitrile and slowly evaporating the solvent at room temperature. Clear, pyramidal or bipyramidal crystals showing 4-fold symmetry (Figure 1) were readily obtained. The melting points of these complexes

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(9) Cambridge Structural Database; Cambridge Crystallographic Data Centre, University Chemical Laboratory: Cambridge, England, October 1993 update; Version 5.4 (Vax).

(10) Gilmore, C. J. *J. Appl. Crystallogr.* **1984**, *17*, 42–46.

(11) Beurskens, P. T. Technical Report, University of Nijmegen: The Netherlands, 1984; Vol. 1.

(12) Mason, R. *Acta. Crystallogr.* **1956**, *9*, 405–410.

Table 3. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters (Å^2) of (Succinimide)$_2$LiI (4) with Esd's in Parentheses

atom	x	y	z	B_{eq}^{a}
I$^-$	$^1/_2$	$^1/_4$	$^1/_8$	3.53(3)
Li$^+$	1	$^3/_4$	$^1/_8$	2.3(3)
N	$^1/_2$	$^3/_4$	0.0562(3)	2.5(2)
C(1)	0.6467(4)	$^3/_4$	0.0943(2)	2.2(1)
C(2)	0.5987(5)	$^3/_4$	0.1686(2)	2.8(1)
O(1)	0.7922(3)	$^3/_4$	0.0689(1)	2.9(1)
H	$^1/_2$	$^3/_4$	0.0077	3.0
H(S)	0.6421	0.6501	0.1908	3.3

^{a} $B_{eq} = {}^1/_3\sum_i\sum_j B_{ij}a_i{}^*a_j{}^*a_ia_j$.

Table 4. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters (Å^2) of (Succinimide)$_2$LiPF$_6$ (7) with Esd's in Parentheses

atom	x	y	z	B_{eq}^{a}
P	$^1/_2$	$^3/_4$	$-^1/_8$	2.80(3)
F(1)	0.6378(4)	0.8878	$-^1/_8$	6.7(2)
F(2)	0.6001(5)	0.8475(5)	−0.1794(2)	6.6(2)
O(1)	0.7819(2)	$^3/_4$	0.0816(1)	3.67(8)
N	$^1/_2$	$^3/_4$	0.0686(1)	2.9(1)
C(1)	0.6430(3)	$^3/_4$	0.1051(1)	2.8(1)
C(2)	0.5952(4)	$^3/_4$	0.1753(1)	3.4(1)
Li$^+$	1	$^3/_4$	$^1/_8$	3.1(2)
H	$^1/_2$	$^3/_4$	0.0227	3.6
H(S)	0.6370	0.6534	0.1971	3.8

^{a} $B_{eq} = {}^1/_3\sum_i\sum_j B_{ij}a_i{}^*a_j{}^*a_ia_j$.

Table 5. Comparative Lithium and Hydrogen-Bond Geometries and Selected Intra- and Intermolecular Bond Lengths for 3, 4, and 7

	3	**4**	**7**
Li–O$_{1,2}$ (Å)	1.966(4), 1.916(4)	1.951(3)	1.965(2)
C$_{1,4}$–N (Å)	1.347(3), 1.382(3)	1.361(4)	1.371(3)
C$_{1,4}$=O (Å)	1.231(3), 1.204(3)	1.234(4)	1.215(3)
H···I (Å)		2.595	
N···I (Å)		3.545(6)	
F···H (Å)			2.221, 3.414
N···F (Å)			3.320(2), 3.072(5)
P···H (Å)			3.035
O–Li–O (deg)	107.20(3) 112.83(7) 109.6(3)	108.45(7) 111.50(2)	101.89(4) 126.0(1)
C–N–C (deg)	113.4(2)	113.6(4)	113.7(3)
N–C=O (deg)	123.5(2), 123.7(2)	123.1(3)	123.4(2)
C=O–Li (deg)	124.5(2), 122.3(2)	122.0(2)	129.6(2)

are well above 200 °C, and these crystals are very stable at ambient temperature. The exact melting points of the crystals could not be determined because these crystals have very broad melting ranges. Complexes 3 and 4 turned brown and started to liquefy at about 270 °C, but maintain some crystallinity until the material turns completely black at about 290 °C. The crystals were soluble in DMSO, water, and methanol but insoluble in acetone and chloroform.

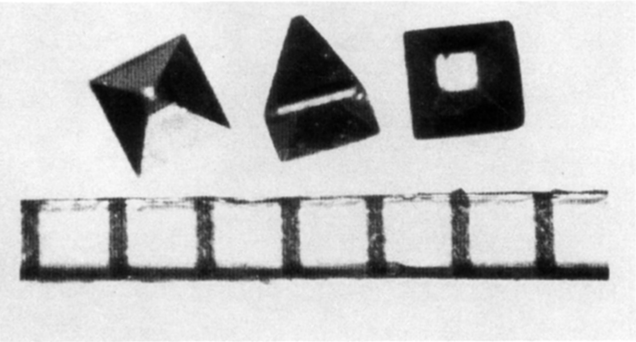


Figure 1. Pyramidal crystals of (succinimide)$_2$LiBF$_4$ grown from a 1:1 methanol/acetonitrile mixture showing 4-fold symmetry. Each division represents 1 mm.

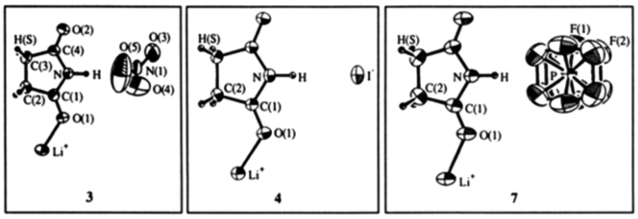
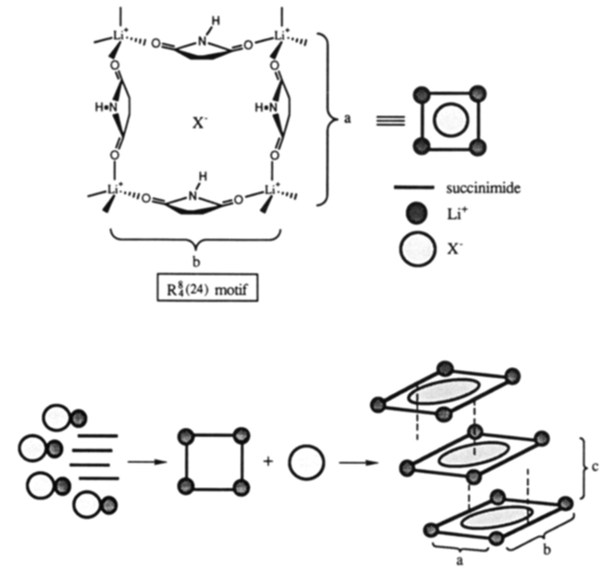


Figure 2. ORTEP drawing of complexes **3**, **4**, and **7** with atom labeling; thermal ellipsoids are at the 50% probability. H(S) indicates succinimide methylene hydrogens. Note that in **7**, the fluorine atoms are disordered over two positions.

Scheme 1



(Succinimide)$_2$LiI (4). In the crystal structure of **4**, the hydrogen-bonded dimers found in homomeric succinimide are disrupted. The asymmetric unit contains $^1/_4$ of a succinimide molecule, $^1/_8$ of a lithium cation, and $^1/_8$ of a iodide anion. Both *anti* lone pairs of electrons of the succinimide carbonyl groups are involved in an ion–dipole interaction with the lithium cation. The complex is composed of infinite chains of succinimide and Li$^+$ along the *a* and *b* axes forming a two-dimensional network (Figure 3a). Lithium ion is tetrahedrally coordinated by four carbonyls of four succinimide molecules, and a strong interaction exists between the lithium cation and the carbonyl group of the succinimide molecule [Li–O = 1.951(3) Å]. The symmetry about the lithium ion is D_{2d}, or the resulting symmetry is slightly distorted from tetrahedral [Li–O–Li = 108.45(7)° and 111.5(2)°]. Each succinimide molecule is puckered. It is also bisected by a mirror plane, and the two methylene carbons are disordered to preserve this mirror plane. Each succinimide molecule forms a bridge between two lithium ions, and four succinimide molecules alternate with four lithium ions to form a 24-membered ring, which has a $R^8_4(24)$ graph set motif[13] (Scheme 1). This recurring pattern is

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[13] (a) Etter, M. C. *Acc. Chem. Res.* **1990**, *23*, 120–126. (b) Etter, M. C.; Macdonald, J. C.; Bernstein, J. *Acta Crystallogr. B46* **1990**, *46*, 256–262. Graph sets are developed to systematically catagorize hydrogen-bond patterns. The notation, $G^a_d(r)$ where G is the pattern designator, r is its degree, and a and d are the number of acceptors and donors, specifies hydrogen-bonding motifs. We have adapted the nomenclature to succinimide–metal salt complexes, where Li$^+$ is a donor.

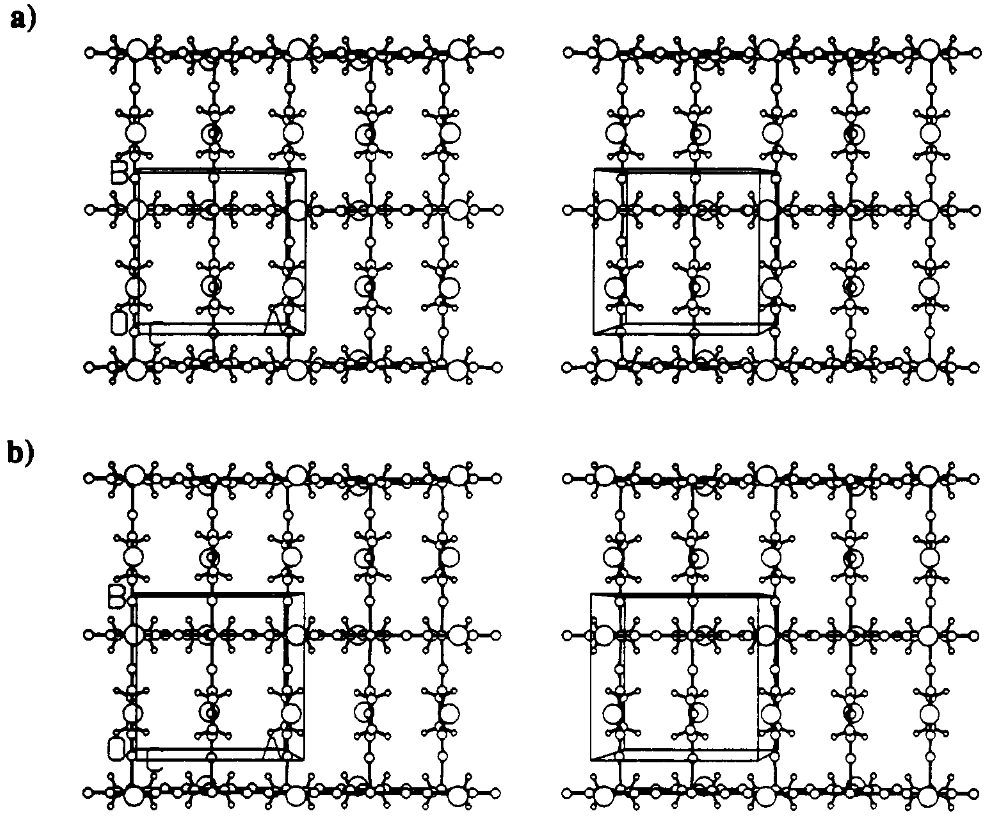

Figure 3. (a) Stereoview of structure 4 approximately along the *c* axis showing the two-dimensional layers of the square ring, R_4^8 (24) graph set motif. (b) Stereoview of structure 7 showing the identical view along the *c* axis. Fluorine atoms are deleted for clarity. The largest circle represent I$^-$ in (a) and phosphorus ion in (b).

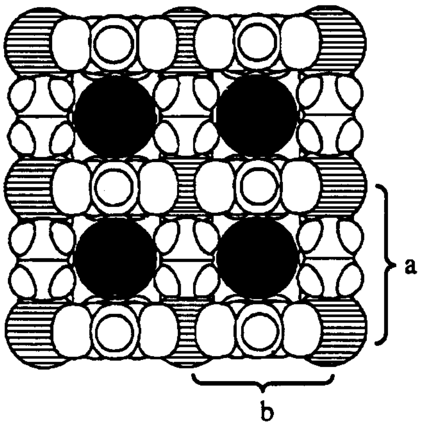

Figure 4. Space-filling model of 4 showing the iodide ion (dark circle) fitting tightly inside the square ring. Lithium cations are shown as striped circles.

Table 6. Unit-Cell Dimensions and Anion Sizes of (Succinimide)$_2$LiX Complexes

		unit-cell dimensions (Å)		
compound	anion	*a* = *b*	*c*	anion size (Å)[2a,14]
1	Cl$^-$	7.649	18.583	1.670
2	Br$^-$	7.685	18.978	1.820
3	NO$_3^-$	7.755	19.657	2.010
4	I$^-$	7.763	19.560	2.060
5	BF$_4^-$	7.830	19.940	2.086
6	ClO$_4^-$	7.880	20.060	2.239
7	PF$_6^-$	8.029	20.550	2.345

found in structures 3 and 7 as well. The iodide ion lies at the center of this 24-membered ring and fits tightly inside it (Figure 4). The layers above and below the shown layer are shifted 1/2 unit cell along the *a* or *b* axis in order to form hydrogen bonds (shown in broken lines) between the imide N–H groups of the above and below layers and the iodide ion (Scheme 1). These two hydrogen-bonding interactions stabilize the complex, and link the structure in three dimensions.

(Succinimide)$_2$LiPF$_6$ (7). Although PF$_6^-$ is larger than I$^-$ (Table 6), the crystal structure of 7 (Figure 3b) is isomorphous with that of 4, while showing the expected increase in the unit-cell dimensions. The asymmetric unit also consists of 1/4 of a succinimide molecule, 1/8 of a lithium cation, and 1/8 of a hexafluorophosphate anion. The main interaction in 7 is between the lithium ion and the carbonyl group [Li–O = 1.965(2) Å]. In structure 7, each fluorine atom in PF$_6^-$ is disordered over two positions giving rise to a total of 12 half-occupying fluorine atoms around the phosphorus atom. Hydrogen bonding exists between the imide hydrogen and the fluoride atoms of the anion. The overall geometry around the lithium ion is a distorted tetrahedron. Four of the O–Li$^+$–O angles are 101.89° and the remaining two angles are 126.0°. The tetrahedral geometry in this structure is more distorted than in 4 (108.45° and 111.5°), presumably due to incorporation of a larger anion.

(Succinimide)$_2$LiNO$_3$ (3). 3 is slightly different from the other two structures. The asymmetric unit consists of one succinimide molecule, one-half of a lithium cation, and one-half of a nitrate anion. Although the interactions between the succinimide molecule and the lithium salt are identical to the previous two structures, 3 crystallizes in a lower symmetry group because the nitrate anion is not as spherical as the I$^-$ or PF$_6^-$ anions (Figure 5). The nitrate anion is disordered and adopts two different orientations within the unit cell (Figure 6). The nitrate anion and the lithium cation lie on a two-fold axis resulting

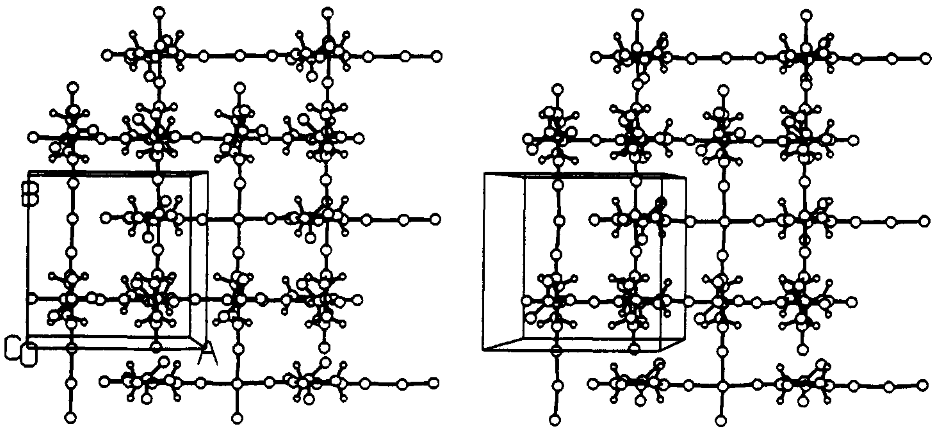

Figure 5. Stereoview of structure 3 approximately along the *c* axis.

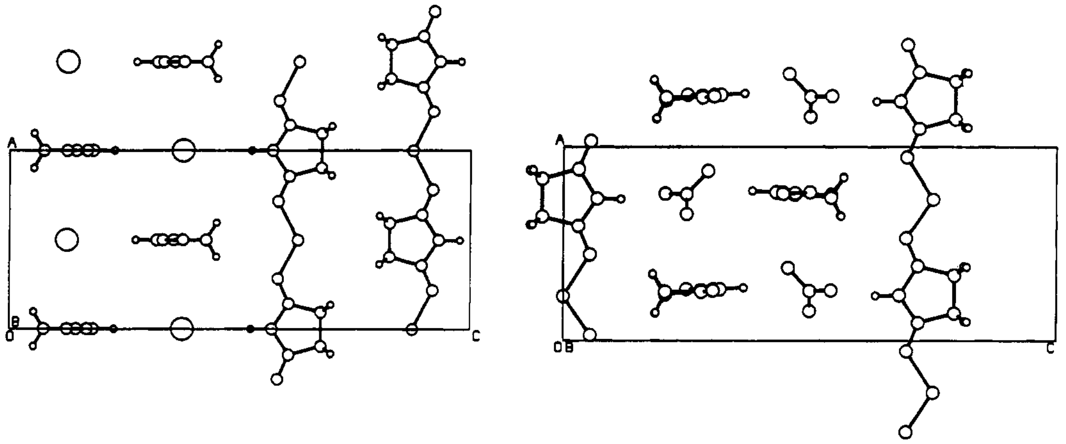

Figure 6. Unit cells of structures 4 and 3 comparing the spherical anion, I^-, and the disk-shaped anion, NO_3^-.

in two different Li–O distances [Li–O(1) = 1.966(4) Å, Li–O(2) = 1.916(4) Å].

Discussion

Other Complexes. Anion radii and unit-cell dimensions of seven succinimide–lithium salt complexes are listed in Table 6. As the size of the anion increases from 1.670 to 2.345 Å, the unit-cell lengths *a* and *b*, which are Li–Li distances, increased by 0.38 Å in both directions with an almost 2.0 Å increase in the *c* axis in order to accommodate larger anions (Scheme 1). The greater variation in the unit cell lengths *c*, which represent the hydrogen-bonded spacing between the $R_4^8(24)$ layers, suggests that this parameter is more flexible. The results indicate that the Li–Li distance is proportional to the size of the anion (Figure 7). The Li–Li distance increases as the size of the anion increases so that the anion can fit inside the 24-membered ring as shown previously. Apparently, F^- (r = 1.14 Å[2a]) is too small and AsF_6^- (r = 2.47 Å[14b]) is too large to be incorporated into the $R_4^8(24)$ ring. The sizes of these anions therefore are critical in the solid-state complexation of succinimide with lithium metal salts.

Comparison of 3, 4, and 7. The major differences between the isostructural complexes 4 and 7 (space group $I4_1/amd$) are the distortion of the tetrahedral geometry about the lithium ion and the Li–O distances. In the case of structure 7, this distortion about the lithium cation is larger and the Li–O distance is slightly longer. The Li–O interaction in 7 appears to be weaker, as reflected by the shorter C=O distance (Table 5).

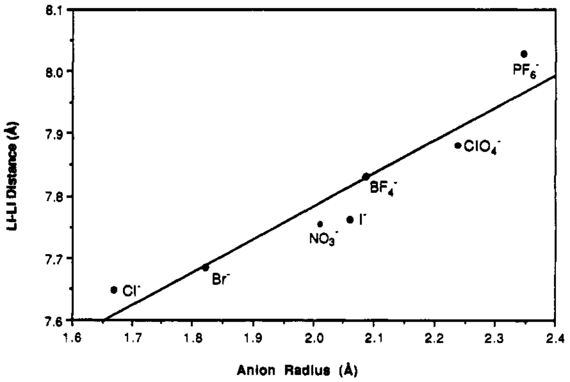

Figure 7. Correlation between the anion size and the Li–Li distance.

Although the overall interactions between the succinimide molecule and the lithium salt are identical to those in the previous structures, structure 3 (space group $P4_12_12$) is in a lower symmetry group (point group 422 versus point group $4/mmm$ for 4 and 7) as a result of the different anion shape. The nitrate anion is disklike, whereas all other anions behave as if spherical, including octahedral PF_6^-.[14] Because of the disorder in oxygen atoms, there are two different orientations of the nitrate anion related by a 2_1 screw axis within the unit cell (Figure 6). The spherical anions such as I^- and PF_6^- have no directionality and thus the orientation of these anions does not affect the crystal symmetry. Structure 3 would be isomorphous

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[14] (a) Schomaker, V.; Waser, F.; Marsh, R. E.; Bergman, G. *Acta Crystallogr.* **1959**, *12*, 600. (b) Mingo, D. M. P.; Rohl, A. L. *Inorg. Chem.* **1991**, *30*, 3769–3771.

with structures 4 and 7 if the nitrate group were disordered to a spherical shape; however, there are distinct orientations of the nitrate anion in the unit cell, resulting in the space group change.

The other four (succinimide)$_2$LiX are crystallographically isomorphous to structures 4 and 7. Morphologies of these crystals are either pyramidal or bipyramidal, which are identical to complexes 4 and 7 as shown in Figure 1. They also crystallize in the highly symmetric and unusual space group, $I4_1/amd$. The size of the unit cell increases as the size of the anion increases. These four structures also contain the $R_4^8(24)$ motif, which is flexible enough to accommodate different sizes of anions.

One of the remarkable features of these complexes is the strong interaction between the carbonyl group and the lithium cation. The driving force for the crystallization in this system appears to be the strong ion–dipole interaction between the imide carbonyl group and the lithium cation. As shown in Scheme 1, $R_4^8(24)$ motif may form first, which in turn, determines the size of anion that can be incorporated into the solid matrix and the final structure of the new intermolecularly stabilized system. The Li–O distances in all three structures are comparable to tetrahedrally coordinated Li^+–carboxylate complexes ($Li\text{–}O_{ave}$ = 1.957 Å)[7] where the interactions are strong electrostatic ion–ion interactions between the Li^+ and the carboxylate oxygen donor atoms.

Lithium salts are known to interact more strongly with the amide group at the carbonyl oxygen than those of other alkali metal salts such as sodium or potassium salts.[15] Such binding of Li^+ to the amide carbonyl oxygen may be of importance in studying the conformational changes of polypeptides and proteins in high salt media. The carbonyl group of succinimide molecules also shows a strong preference for Li^+. Attempts to form succinimide complexes with a series of metal salts (NaF, NaCl, NaBr, NaI, $NaPF_6$, KCl, KBr, KI, $MgBr_2$, $MgSO_4$, $CaBr_2$) were unsuccessful. Monovalent cations such as Na^+ and K^+ with ionic radii of 1.16 and 1.52 Å,[2a] respectively, are much larger than Li^+ and the oxophilicity decreases as the radii of cations increases. Na^+ and K^+ are, in most cases, octahedrally coordinated whereas Li^+ forms 4- or 5-fold coordinated[7] complexes because of its small cavity radius for binding. The complexation phenomenon between succinimide and lithium metal salts described here is influenced equally by the size of the $R_4^8(24)$ ring and the anions that can fit into this ring. Na^+ or K^+ is unlikely to form the $R_4^8(24)$ ring of a reasonable size with succinimide, and thus no complex is formed. Divalent cations, Mg^{2+} and Ca^{2+} with ionic radii of 0.86 and 1.14 Å[2a] also form complexes with coordination number greater than four.[4] Although Mg^{2+} is comparable in size to Li^+, the tendency of preferred higher coordination number (≥6) for these ions may explain the non-complexing behavior of Mg^{2+} and Ca^{2+} salts with succinimide.

Conclusions

We have demonstrated that the hydrogen-bonded dimers found in succinimide are disrupted in its complexation with lithium metal salts through an ion–dipole interaction. The imide carbonyls chelate the Li^+ cation forming orthogonal infinite chains linking into $R_4^8(24)$ motifs in a two-dimensional sheet. Intermolecular hydrogen bonds between the imide N–H hydrogen and the anion link the molecules in the third dimension. The difference in the three crystal structures reported here resulted from varying anion sizes and shapes. Other lithium salts, such as $LiBF_4$, $LiClO_4$, LiBr, and LiCl, which are crystallographically isomorphous to structures 4 and 7, showed a good correlation between the anion size and the Li–Li distance, indicating that these lithium–succinimide complexes are flexible enough in structure to accommodate a variety of anions. These results show that intermolecular ion–dipole interactions compete with the preformed hydrogen-bond network of succinimide, causing specific reorganization to accommodate metal ions. From these investigations, we have shown that cocrystallization experiments are a useful way to demonstrate the molecular recognition properties of classes of molecules and to evaluate the strengths of intermolecular forces in weakly associated systems. This strategy can be extended to evaluate the molecular recognition properties of other functional groups and may aid in designing bulk materials with desirable properties.

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Supplementary Material Available: Details of the three crystal structural analyses including intra- and intermolecular bond lengths and angles (18 pages); tables of observed and calculated structure factors (21 pages). Ordering information is given on any current masthead page.

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(15) Balasubramanian, D.; Shaikh, R. *Biopolymers* **1973**, *12*, 1639–1650.