

Coordination of the new weakly coordinating anions $\text{Al}(\text{OCH}(\text{CF}_3)_2)_4^-$, $\text{Al}(\text{OC}(\text{CH}_3)(\text{CF}_3)_2)_4^-$, and $\text{Al}(\text{OC}(\text{Ph})(\text{CF}_3)_2)_4^-$ to the monovalent metal ions Li^+ and Tl^+

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Abstract

The structures of Li^+ or Tl^+ salts of three new fluoroalkoxide-containing aluminate anions were determined by X-ray crystallography. For $\text{LiAl}(\text{OC}(\text{Ph})(\text{CF}_3)_2)_4$, monoclinic, $C2/c$, $a = 42.297(6)$, $b = 10.641(1)$, $c = 19.132(2)$ Å, $\beta = 114.808(9)^\circ$, $Z = 8$, $T = -100^\circ\text{C}$, $R = 0.052$; for $\text{TlAl}(\text{OC}(\text{CH}_3)(\text{CF}_3)_2)_4$, monoclinic, $P2_1/c$, $a = 12.650(3)$, $b = 9.970(2)$, $c = 21.237(4)$ Å, $\beta = 94.00(3)^\circ$, $Z = 4$, $T = -100^\circ\text{C}$, $R = 0.073$; for $\text{TlAl}(\text{OCH}(\text{CF}_3)_2)_4$, monoclinic, $P2_1/n$, $a = 14.261(1)$, $b = 9.8024(9)$, $c = 16.911(2)$ Å, $\beta = 93.467(8)^\circ$, $Z = 4$, $T = -130^\circ\text{C}$, $R = 0.053$. The monatomic, monovalent cations interact with their respective anions by means of M–O and M–F bonds. The Tl^+ cations in $\text{TlAl}(\text{OCH}(\text{CF}_3)_2)_4$ and $\text{TlAl}(\text{OC}(\text{CH}_3)(\text{CF}_3)_2)_4$ interact with three different aluminate anions. The Li^+ cation in $\text{LiAl}(\text{OC}(\text{Ph})(\text{CF}_3)_2)_4$ interacts with only one aluminate anion, forming a rare trigonal–prismatic LiO_2F_4 coordination unit. © 1998 Elsevier Science B.V.

Keywords: Weakly coordinating anion; Fluoroanion; Fluoroalkoxide; Alkoxide; Lithium; Thallium; Bond valence

1. Introduction

Investigations of very reactive metal and nonmetal cations continue to spur the development of new weakly coordinating anions (WCA's) [1–3]. One of the most important uses of WCA's is to enhance the catalytic activity of metal cations. Two examples that have received considerable attention recently are metallocene-catalyzed olefin polymerization [4–7] and lithium-catalyzed Diels–Alder reactions and 1,4-conjugate addition reactions [8–13]. Useful anions must not only be weakly coordinating,

they must also be stable with respect to oxidation and/or fragmentation in the presence of highly electrophilic cations. In addition, an ideal WCA should have a single negative charge dispersed over a large surface composed of relatively nonpolar bonds to weakly basic atoms such as hydrogen or the halogens. Weakly coordinating anions which conform to many, if not all, of these criteria include $\text{B}(\text{Ar}_f)_4^-$ ($\text{Ar}_f = \text{C}_6\text{F}_5$ [5,14–18] or $3,5\text{-C}_6\text{H}_3(\text{CF}_3)_2$) [19,20]), $\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})_2^-$ [8], $\text{CB}_{11}\text{H}_{12-n}\text{X}_n^-$ ($\text{X} = \text{H}$ [21], F [22], Cl [23], Br [23], and I [24]), $\text{CB}_9\text{H}_{10-n}\text{X}_n^-$ ($\text{X} = \text{H}$ [25], F [26], Cl [27], Br [28]), and $\text{M}(\text{OTeF}_5)_n^-$ ($n = 4$, $\text{M} = \text{B}$; $n = 6$, $\text{M} = \text{Nb}$, Sb) [29].

We are investigating a new and potentially large class of WCA's based on polyfluorinated

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alkoxide substituents, $M(OR_f)_n^-$. Potential advantages of such homoleptic anions include (1) peripheral fluorine atoms with lower Lewis basicity than the fluorine atoms in anions containing B–F or Te–F bonds, (2) a high degree of compositional flexibility due to the wide variety of readily available polyfluorinated alcohols, and (3) relatively low cost. Anions such as $M(OR_f)_n^-$ have not been extensively investigated: although there are many examples of metal and nonmetal complexes containing polyfluoroalkoxide ligands [30–32], there are only five reported homoleptic polyfluoroalkoxide anions. These are $Y(OC(CH_3)(CF_3)_2)_5^{2-}$ [33], $Y(OCH(CF_3)_2)_6^{3-}$ [33], $Zr(OCH(CF_3)_2)_6^{2-}$ [34], $Nb(OCH(CF_3)_2)_6^-$ [35], and $Cu(OCH(CF_3)_2)_4^{2-}$ [36].

We recently prepared four new fluoroalkoxide-containing anions, $B(OCH(CF_3)_2)_4^-$, $Al(OCH(CF_3)_2)_4^-$, $Al(OC(CH_3)(CF_3)_2)_4^-$, and $Al(OC(Ph)(CF_3)_2)_4^-$ [37]. In this paper we report the structures of salts of $Al(OCH(CF_3)_2)_4^-$ and $Al(OC(CH_3)(CF_3)_2)_4^-$ with the large cation Tl^+ and the salt of $Al(OC(Ph)(CF_3)_2)_4^-$ with the small cation Li^+ . The structures are analyzed using the bond–valence method, and conclusions about their weakly coordinating nature are presented. A preliminary report of the structure of $LiAl(OC(Ph)(CF_3)_2)_4$ has appeared [13].

2. Experimental

The compounds $LiAl(OC(Ph)(CF_3)_2)_4$, $TlAl(OC(CH_3)(CF_3)_2)_4$, and $TlAl(OCH(CF_3)_2)_4$ were prepared as previously described [37] and were handled with rigorous exclusion of air and water [38]. Crystals of $LiAl(HFPP)_4$ were grown by cooling a hexane solution to -40°C . Crystals of $TlAl(HFTB)_4$ were grown by slow evaporation of solvent from a benzene/hexane solution. Crystals of $TlAl(HFIP)_4$ were grown by vacuum sublimation at 60°C . The crystals were examined at -20°C or colder using an apparatus previously described [39]. When a suitable crystal was found, it was embedded in Halocar-

bon 25-5S grease at the end of a glass fiber and quickly placed in the cold nitrogen stream of the diffractometer LT-2 low-temperature unit. Details of the crystallographic experiment and subsequent computations are summarized in Table 1 [40].

The diffraction data were obtained in all three cases using a Siemens *P4* diffractometer, and computations were performed with crystallographic software supplied by Siemens, much of which was written by Professor Sheldrick [40]. Lorentz and polarization corrections were applied to the data, and empirical absorption corrections were applied based on psi-scan data.

The structures were all solved by direct methods and refined using full-matrix least-squares procedures on F^2 for all data. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included in idealized positions in each case. Selected interatomic distances and angles are listed in Table 2.

3. Results

3.1. Structure of $LiAl(HFPP)_4$ (Tables 3–7)

The structure of this compound, shown in Fig. 1, consists of discrete $LiAl(OC(Ph)(CF_3)_2)_4$ molecules composed of lithium(1+) and aluminate(1-) ions in a configuration best described as a penetrated ion pair [41]. There are no significant intermolecular contacts. The Al atom is tetrahedrally coordinated by four 1,1,1,3,3,3-hexafluoro-2-phenyl-2-propoxide ($HFPP^-$) ligands. The O1–Al–O2 angle of $91.8(1)^\circ$ is smaller than the five other O–Al–O angles. The O3–Al–O4 angle, which is the only O–Al–O angle not affected by the coordination of the Li^+ ion, is $105.4(1)^\circ$, close to the ideal tetrahedral angle of 109.5° . The other four O–Al–O angles range from $112.5(1)$ to $116.7(1)^\circ$. The two alkoxide oxygen atoms that bridge the aluminum and lithium atoms form Al–O bonds

Table 1

Details of the X-ray diffraction studies of LiAl(HFPP)₄, TlAl(HFTB)₄, and TlAl(HFIP)₄^a

Compd	LiAl(HFPP) ₄	TlAl(HFTB) ₄	TlAl(HFIP) ₄
Molecular formula	C ₃₆ H ₂₀ AlF ₂₄ LiO ₄	C ₁₆ H ₁₂ AlF ₂₄ O ₄ Tl	C ₁₂ H ₄ AlF ₂₄ O ₄ Tl
Formula wt (g mol ⁻¹)	1006.4	955.6	899.5
Space group	C2/c	P2 ₁ /c	P2 ₁ /n
Unit cell dimensions:			
<i>a</i> (Å)	42.297(6)	12.650(3)	14.261(1)
<i>b</i> (Å)	10.641(1)	9.970(2)	9.8024(9)
<i>c</i> (Å)	19.132(2)	21.237(4)	16.911(2)
<i>β</i> (deg)	114.808(9)	94.00(3)	93.467(8)
Unit cell volume (Å ³)	7817(2)	2672(1)	2359.6(4)
<i>Z</i>	8	4	4
Calcd density (g cm ⁻³)	1.71	2.38	2.53
Cryst dims (mm)	0.60 × 0.46 × 0.12	0.24 × 0.14 × 0.02	0.48 × 0.28 × 0.28
Data collection temperature (°C)	-100(2)	-100(2)	-130(2)
Radiation (λ, Å)	Mo K _α (0.7107)	Mo K _α (0.7107)	Mo K _α (0.7107)
Monochromator	graphite	graphite	graphite
Abs coeff (cm ⁻¹)	0.21	6.27	7.09
Scan type	θ-2θ	θ-2θ	θ-2θ
2θ range (deg)	4–50	4–50	4–60
Reflections	<i>h, k, ± l</i>	<i>h, k, ± l</i>	<i>h, k, ± l</i>
Total No. of reflections meas.	6983	4946	6768
Total unique reflections	6883	4707	5439
<i>R</i> (<i>I</i> > 2σ(<i>I</i>))	0.052	0.073	0.053
<i>wR</i> ^{2b}	0.128	0.176	0.126
GOF	1.04	1.06	1.03

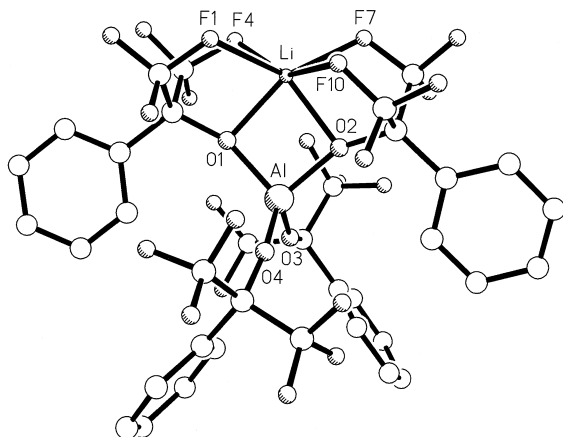
^aHFPP⁻ = OC(Ph)(CF₃)₂⁻; HFTB⁻ = OC(CH₃)(CF₃)₂⁻; HFIP⁻ = OCH(CF₃)₂⁻.^b*wR*² = [[Σ[w(F_o² - F_c²)²]/[Σw(F_o²)²]]^{1/2}, for all data.

Fig. 1. Drawing of the structure of LiAl(OC(Ph)(CF₃)₂)₄ (hydrogen atoms omitted for clarity). The unlabeled shaded circles are fluorine atoms, while the unlabeled open circles are carbon atoms. Selected interatomic distances (Å) and angles (deg): Li–O1, 1.978(8); Li–O2, 1.966(8); Li–F1, 1.984(9); Li–F4, 2.354(10); Li–F7, 2.098(11); Li–F10, 2.082(9); O1–Li–O2, 79.9(3).

of 1.755(3) and 1.773(2) Å, which are considerably longer than the other two terminal Al–O bonds of 1.687(3) and 1.706(3) Å.

The Al(HFPP)₄⁻ aluminate anion acts as a

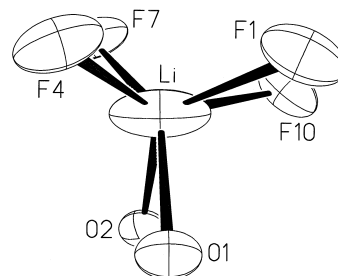


Fig. 2. Drawing of the trigonal-prismatic LiO₂F₄ coordination sphere in LiAl(OC(Ph)(CF₃)₂)₄ (50% probability ellipsoids). The planes formed by O₁-F₁-F₄ and O₂-F₇-F₁₀ triangles make a dihedral angle of 12°. These two triangular planes are twisted away from the ideal, eclipsed conformation by 13°.

hexadentate chelating ligand for the Li^+ cation. The O1–Al–O2 unit forms a four-membered chelate ring with Li^+ , with Li–O bond distances of 1.966(8) and 1.978(8) Å and a O1–Li–O2 bond angle of 79.9(3)°. Four C–F bonds from four different CF_3 groups form five-membered $\overline{\text{O-Li-F-C-C}}$ chelate rings, with Li–F bond distances of 1.984(9), 2.082(9), 2.098(11), and

2.354 (10) Å. The next shortest Li \cdots F contact is greater than 3.5 Å. The overall LiO_2F_4 coordination sphere can best be described as trigonal prismatic; the least-squares planes formed by the $\overline{\text{O1-F1-F4}}$ and $\overline{\text{O2-F7-F10}}$ triangles make a dihedral angle of only 12°. These two triangular planes are twisted away from the ideal, eclipsed conformation by only 13°, as shown in Fig. 2.

Table 2

Selected interatomic distances (Å) and angles (deg) for $\text{LiAl}(\text{HFPP})_4$, $\text{TlAl}(\text{HFTB})_4$, and $\text{TlAl}(\text{HFIP})_4^a$

	$\text{LiAl}(\text{HFPP})_4$	$\text{TlAl}(\text{HFTB})_4$	$\text{TlAl}(\text{HFIP})_4$
M–O1	1.978(8) ^b	2.731(9) ^c	2.805(6) ^c
M–O2	1.966(8) ^b	2.717(9) ^c	2.855(6) ^c
Tl–O3 ^d			2.992(6)
Al–O1	1.773(2)	1.78(1)	1.744(6)
Al–O2	1.755(3)	1.78(1)	1.738(6)
Al–O3	1.687(3)	1.70(1)	1.757(6)
Al–O4	1.706(3)	1.70(1)	1.702(7)
M–F1	1.984(9) ^b	3.087(10) ^c	3.090(7) ^c
M–F4	2.354(10) ^b	2.903(9) ^c	3.398(7) ^c
M–F7	2.098(11) ^b	2.952(10) ^c	3.540(6) ^c
M–F10	2.082(9) ^b	3.081(11) ^c	2.967(6) ^c
Tl–F ^d		3.154(10) (F19')	3.045(6) (F16')
Tl–F ^d		3.240(10) (F11')	3.153(6) (F8')
Tl–F ^d		3.339(10) (F2')	3.245(6) (F13')
Tl–F ^e		3.341(12) (F20'')	3.242(5) (F16'')
Tl–F ^e		3.471(10) (F19'')	
C–F(M) ^f	1.341(5)–1.384(5) ^b	1.31(2)–1.35(2) ^c	1.33(1)–1.34(1) ^c
C–F ^g	1.29(2)–1.35(2)	1.27(2)–1.37(2)	1.29(1)–1.35(1)
C–F1–M	113.4(3) ^b	115.9(9) ^c	114.7(5) ^c
C–F4–M	106.0(3) ^b	115.5(9) ^c	112.5(6) ^c
C–F7–M	109.3(3) ^b	116.6(8) ^c	111.1(5) ^c
C–F10–M	111.0(3) ^b	114.4(9) ^c	120.7(6) ^c
O1–Al–O2	91.8(1)	94.0(5)	95.8(3)
O1–Al–O3	115.8(1)	115.2(5)	111.1(3)
O1–Al–O4	112.5(1)	111.2(5)	116.5(3)
O2–Al–O3	114.8(1)	113.0(5)	111.6(3)
O2–Al–O4	116.7(1)	113.1(5)	118.3(4)
O3–Al–O4	105.4(1)	109.6(5)	103.7(3)
O1–M–O2	79.9(3) ^b	57.9(3) ^c	54.3(2) ^c
F1–M–F4	75.7(3) ^b	53.1(3) ^c	50.3(2) ^c
F1–M–F7	129.5(4) ^b	150.6(3) ^c	152.2(2) ^c
F1–M–F10	99.4(5) ^b	100.8(3) ^c	119.8(2) ^c
F4–M–F7	81.2(4) ^b	148.1(3) ^c	124.3(2) ^c
F4–M–F10	149.1(4) ^b	152.2(3) ^c	154.3(2) ^c
F7–M–F10	78.8(3) ^b	52.7(3) ^c	50.6(2) ^c

^a $\text{HFPP}^- = \text{OC}(\text{Ph})(\text{CF}_3)_2^-$; $\text{HFTB}^- = \text{OC}(\text{CH}_3)(\text{CF}_3)_2^-$; $\text{HFIP}^- = \text{OCH}(\text{CF}_3)_2^-$.

^b M = Li.

^c M = Tl.

^d Bonded to first neighboring molecule.

^e Bonded to second neighboring molecule.

^f Range of C–F values for those fluorines bonded to M.

^g Range of C–F values for those fluorines that are not bonded to M.

Note that a twist angle of 60° would give rise to an octahedral coordination geometry. Another view of the LiO_2F_4 coordination sphere is shown in Fig. 3.

3.2. Structure of $\text{TlAl}(\text{HFTB})_4$ (Tables 2, 8–12)

The structure of this compound, shown in Fig. 4, consists of $\text{TlAl}(\text{OC}(\text{CH}_3)(\text{CF}_3)_2)_4$ ion pairs with five additional Tl–F intermolecular

Table 3
Crystal data and structure refinement for $\text{LiAl}(\text{OC}(\text{Ph})(\text{CF}_3)_2)_4$

Identification code	shs76
Empirical formula	$\text{C}_{36}\text{H}_{20}\text{AlF}_{24}\text{LiO}_4$
Formula weight	1006.44
Temperature	173 (2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	C2/c
Unit cell dimensions	$a = 42.297(6)$ Å $\alpha = 90^\circ$ $b = 10.641(1)$ Å $\beta = 114.808(9)^\circ$ $c = 19.132(2)$ Å $\gamma = 90^\circ$
Volume, Z	$7817(2)$ Å ³ , 8
Density (calculated)	1.710 Mg/m ³
Absorption coefficient	0.207 mm ⁻¹
$F(000)$	4000
Crystal size	0.60 x 0.46 x 0.12 mm
θ range for data collection	2.12 to 25.00°
Limiting indices	$0 \leq h \leq 50$, $0 \leq k \leq 12$, $-22 \leq l \leq 20$
Reflections collected	6983
Independent reflections	6883 ($R_{\text{int}} = 0.0723$)
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6883 / 0 / 596
Goodness-of-fit on F^2	0.759
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0518$, $wR_2 = 0.1158$
R indices (all data)	$R_1 = 0.1052$, $wR_2 = 0.1284$
Extinction coefficient	0
Largest diff. peak and hole	0.311 and -0.315 eÅ ⁻³

contacts. The Al atom is tetrahedrally coordinated by four 1,1,1,3,3,3-hexafluoro-2-methyl-2-propoxide (HFTB⁻) ligands. The O1–Al–O2 angle of 94.0(5)° is smaller than the five other O–Al–O angles. The unconstrained O3–Al–O4 angle is 109.6(5)° and the other four O–Al–O angles range from 111.2(5) to 115.2(5)°. The two Al–O(TI) bond distances are both 1.78(1)

and the two terminal Al–O bond distances are both 1.70(1) Å.

The Al(HFTB)₄⁻ aluminate anion acts as a hexadentate chelating ligand for the Tl⁺ cation in a related manner to that observed for LiAl(HFPP)₄. The O1–Al–O2 unit forms a four-membered chelate ring with Tl⁺, with Tl–O bond distances of 2.717(9) and 2.731(9) Å and a

Table 4

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for LiAl(OC(Ph)(CF₃)₂)₄

	x	y	z	U (eq)
Li	1840 (2)	1054 (10)	52 (4)	75 (3)
O(1)	1772 (1)	1776 (2)	931 (1)	28 (1)
O(2)	1406 (1)	1994 (3)	-503 (1)	37 (1)
O(3)	1401 (1)	4163 (2)	410 (2)	30 (1)
O(4)	1036 (1)	2137 (2)	500 (2)	32 (1)
Al	1386 (1)	2582 (1)	334 (1)	23 (1)
C(1)	2081 (1)	1644 (4)	1586 (2)	30 (1)
C(2)	1324 (1)	1831 (4)	-1275 (2)	31 (1)
C(3)	1346 (1)	5431 (3)	352 (2)	29 (1)
C(4)	824 (1)	1222 (4)	595 (2)	28 (1)
C(5)	2173 (1)	233 (4)	1598 (2)	41 (1)
C(6)	2349 (1)	2444 (4)	1440 (2)	38 (1)
C(7)	1642 (1)	2312 (5)	-1387 (3)	45 (1)
C(8)	1289 (1)	388 (4)	-1413 (2)	40 (1)
C(9)	1550 (1)	5965 (4)	-79 (3)	48 (1)
C(10)	1495 (1)	5960 (4)	1181 (3)	40 (1)
C(11)	1029 (1)	-18 (4)	799 (2)	32 (1)
C(12)	502 (1)	1127 (4)	-183 (2)	36 (1)
C(13)	2068 (1)	2006 (4)	2341 (2)	29 (1)
C(14)	1793 (1)	2704 (5)	2354 (2)	49 (1)
C(15)	1787 (1)	3079 (5)	3032 (3)	63 (2)
C(16)	2047 (1)	2731 (5)	3720 (3)	56 (1)
C(17)	2322 (1)	2074 (5)	3723 (3)	67 (2)
C(18)	2334 (1)	1709 (5)	3048 (3)	56 (1)
C(19)	993 (1)	2501 (4)	-1838 (2)	32 (1)
C(20)	808 (1)	3270 (4)	-1569 (2)	42 (1)
C(21)	519 (1)	3901 (5)	-2066 (3)	58 (1)
C(22)	404 (1)	3757 (5)	-2847 (3)	61 (2)
C(23)	586 (1)	2994 (5)	-3126 (3)	67 (2)
C(24)	880 (1)	2368 (4)	-2622 (2)	51 (1)
C(25)	955 (1)	5794 (4)	-47 (2)	27 (1)
C(26)	840 (1)	6951 (4)	-409 (2)	39 (1)
C(27)	486 (1)	7241 (5)	-707 (2)	47 (1)
C(28)	250 (1)	6424 (5)	-667 (2)	47 (1)
C(29)	362 (1)	5271 (4)	-309 (2)	40 (1)
C(30)	714 (1)	4966 (4)	-3 (2)	34 (1)
C(31)	710 (1)	1578 (4)	1228 (2)	34 (1)
C(32)	826 (1)	2685 (4)	1636 (2)	43 (1)
C(33)	724 (1)	3016 (5)	2215 (3)	60 (2)
C(34)	507 (1)	2251 (7)	2379 (3)	69 (2)
C(35)	389 (1)	1147 (6)	1981 (3)	60 (2)
C(36)	489 (1)	811 (5)	1417 (3)	45 (1)

Table 4 (continued)

F(1)	2117(1)	-156(2)	869(1)	57(1)
F(2)	2507(1)	-31(2)	2034(1)	53(1)
F(3)	1981(1)	-487(2)	1817(2)	55(1)
F(4)	2363(1)	2127(3)	776(1)	56(1)
F(5)	2261(1)	3648(2)	1385(2)	51(1)
F(6)	2673(1)	2370(3)	1993(1)	54(1)
F(7)	1938(1)	1776(3)	-859(2)	62(1)
F(8)	1637(1)	2080(3)	-2070(2)	64(1)
F(9)	1677(1)	3541(3)	-1265(2)	71(1)
F(10)	1564(1)	-205(2)	-826(1)	59(1)
F(11)	1292(1)	0(2)	-2053(1)	52(1)
F(12)	1008(1)	-47(2)	-1366(2)	57(1)
F(13)	1390(1)	5717(3)	-832(2)	58(1)
F(14)	1868(1)	5453(2)	166(2)	57(1)
F(15)	1600(1)	7212(2)	-3(2)	67(1)
F(16)	1835(1)	5743(2)	1560(1)	54(1)
F(17)	1342(1)	5396(2)	1585(1)	49(1)
F(18)	1446(1)	7193(2)	1209(2)	57(1)
F(19)	1287(1)	48(2)	1499(1)	41(1)
F(20)	835(1)	-1015(2)	791(1)	46(1)
F(21)	1174(1)	-276(2)	312(1)	38(1)
F(22)	279(1)	231(2)	-202(1)	53(1)
F(23)	329(1)	2208(2)	-347(1)	52(1)
F(24)	589(1)	875(3)	-763(1)	53(1)

$U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

very acute O1–Ti–O2 bond angle of 57.9(3)°. Four C–F bonds from four different CF₃ groups form five-membered $\overline{\text{O-Ti-F-C-C}}$ chelate rings, with Ti–F bond distances of 2.903(9), 2.95(1), 3.08(1), and 3.09(1) Å. Unlike the LiO₂F₄ coordination unit described above, the TiO₂F₄ unit in TiAl(HFIB)₄, which is shown in Fig. 3, is only approximately one hemisphere of the total TiO₂F₉ coordination sphere. The remaining five Ti–F contacts come from two additional Al(HFTB)₄[−] anions. These Ti–F distances range from 3.154(10) to 3.471(10) Å. The next shortest Ti···F contact is greater than 4.1 Å. The least-squares planes formed by the $\overline{\text{O1-F1-F4}}$ and $\overline{\text{O2-F7-F10}}$ triangles make a dihedral angle of 111°, nearly 100° larger than the corresponding angle in LiAl(HFPP)₄.

3.3. Structure of TiAl(HFIP)₄ (Tables 2, 13–17)

The structure of this compound, shown in Fig. 5, consists of TiAl(OC(H)(CF₃)₂)₄ ion pairs with one additional Ti–O intermolecular contact

and four additional Ti–F intermolecular contacts. The Al atom is tetrahedrally coordinated by four 1,1,1,3,3,3-hexafluoro-2-propoxide (HFIP[−]) ligands. The O1–Al–O2 angle of 95.8(3)° is smaller than the five other O–Al–O angles. There are no unconstrained O–Al–O angles due to the formation of the intermolecular Ti′–O3 contact. Nevertheless, the O3–Al–O4 angle of 103.7(3) is significantly smaller than the remaining four O–Al–O angles, which range from 111.1(3) to 118.3(4)°. The three Al–O(Ti) bond distances are 1.744(6), 1.738(6), and 1.757(6), and the terminal Al–O bond distance (Al–O4) is 1.702(7) Å.

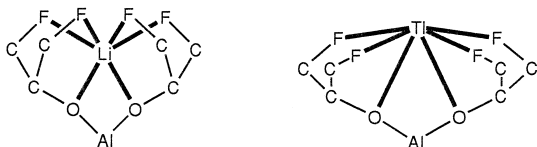
The Al(HFIP)₄[−] aluminate anion acts as a hexadentate chelating ligand for the Ti⁺ cation in a manner similar to that observed for TiAl(HFTB)₄. The O1–Al–O2 unit forms a four-membered chelate ring with Ti⁺, with Ti–O bond distances of 2.805(6) and 2.855(6) Å and a very acute O1–Ti–O2 bond angle of 54.3(2)°. Four C–F bonds from four different CF₃ groups form five-membered $\overline{\text{O-Ti-F-C-C}}$ chelate rings, with

Tl–F bond distances of 2.967(6), 3.090(7), 3.398(7), and 3.540(0) Å. Like the TlO_2F_4 coordination unit in $\text{TlAl}(\text{HFTB})_4$, the TlO_2F_4 unit in $\text{TlAl}(\text{HFIB})_4$, which is shown in Fig. 3, is approximately one hemisphere of the total TlO_3F_8 coordination sphere. The remaining Tl–O (2.992(6) Å) and Tl–F contacts (3.045(6) to 3.245(6) Å) come from two additional $\text{Al}(\text{HFIP})_4^-$ anions. The next shortest Tl...F contact is greater than 4.1 Å. The least-squares planes formed by the $\text{O}_1\text{–F}_1\text{–F}_4$ and $\text{O}_2\text{–F}_7\text{–F}_{10}$ triangles make a dihedral angle of 85° , approximately 25° smaller than the corresponding angle in $\text{TlAl}(\text{HFTB})_4$.

4. Discussion

4.1. Coordination of $\text{Al}(\text{OR}_f)_4^-$ to Li^+ and Tl^+

All three aluminate anions are composed of an Al^{3+} ion surrounded by a tetrahedral array of oxygen atoms from four 1,1,1,3,3,3-hexafluoro-2-R-2-propoxide ligands. The substituents R for $\text{Al}(\text{HFIP})_4^-$, $\text{Al}(\text{HFTB})_4^-$, and $\text{Al}(\text{HFPP})_4^-$ are H, CH_3 , and Ph, respectively. Each aluminate coordinates to one primary monovalent metal ion, either Li^+ or Tl^+ , with the same six-atom donor set, O1, O2, F1, F4, F7, F10, forming a set of five chelate rings depicted in the structures below.



There are several unusual and noteworthy features about the coordination environment of the Li^+ cation in $\text{LiAl}(\text{HFPP})_4$. The first is that the Li^+ is roughly trigonal prismatic. Compared with four- and five-coordination, six-coordination is relatively uncommon for Li^+ [42], but, more importantly, six-coordinate Li^+ ions are generally octahedral. Examples include LiF [43], $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$ [44], $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$ [45], LiSbF_6 [46], $\text{Li}(\text{en})_3\text{I}$ (en = ethylenediamine) [47], and

$\text{Li}(\text{C}_6\text{H}_5\text{O}_7) \cdot 5\text{H}_2\text{O}$ ($\text{C}_6\text{H}_5\text{O}_7^{3-}$ = citrate) [48]. The trigonal prismatic coordination about Li^+ is probably brought about by two geometric constraints of the hexadentate, chelating $\text{Al}(\text{HFPP})_4^-$ anion. The first constraint is the rigidity of the four-membered $\text{Li-O}_1\text{-Al-O}_2$ chelate ring. The second constraint is that the two five-membered chelate rings formed by each of the two alkoxide substituents do not have a common atom that is also coordinated to Li^+ , unlike the more flexible hexadentate ligand EDTA^{4-} .

The second noteworthy feature is the presence of, and the nature of, the four $\text{Li-F}(\text{C})$ bonds in $\text{LiAl}(\text{HFPP})_4$. Carbon–halogen bonds are very poor Lewis bases [49], yet four of the six ligands bound to Li^+ are fluorine atoms bonded to sp^3 carbon atoms. This is the first example of a compound with more than two $\text{Li-F}(\text{C})$ bonds for a given Li^+ ion and the first example in which a majority of atoms coordinated to Li^+ are organofluorine atoms. Furthermore, the 1.984(9) Å Li-F_1 distance is shorter than any previously reported $\text{Li-F}(\text{C})$ distances [49,50]. For comparison, the $\text{Li-F}(\text{C})$ distances in $[\text{Li}(\text{FN}_2\text{O}_3)][\text{ClO}_4]$ [50], $\text{Li}(2,4,6\text{-C}_6\text{H}_2(\text{CF}_3)_3)(\text{Et}_2\text{O})$ [51] and $\text{Li}(\text{C}_6\text{F}_5\text{NSiF}(t\text{-Bu})_2)(\text{THF})_2$ [52] are 2.035(5), 2.25(1) (average of two distances) and 2.27(1) Å, respectively, and the Li-F distance in crystalline LiF is 2.009 Å [43]. The Li-F_1 bond, at least, cannot be considered a secondary [53] bond: the Li-F_1 distance is the same, to within $\pm 3\sigma$, as the two Li-O distances.

Another noteworthy feature is that the $\text{Li-F}(\text{C})$ bonds are sufficiently strong to significantly lengthen the $\text{C-F}(\text{Li})$ bonds (1.341(5)–1.384(5) Å) relative to the other C-F bonds (1.298(5)–1.342(5) Å) in $\text{LiAl}(\text{HFPP})_4$. A plot of $\text{Li-F}(\text{C})$ vs. C-F bond distance and a plot of all 24 C-F bond distances are shown in Fig. 6 (the errors are shown at the $\pm 3\sigma$ level of confidence). The upper plot in Fig. 6 suggests the sensible correlation that the C-F bonds are lengthened, and presumably weakened, as the fluorine atoms coordinate more strongly to the Li^+ ion. This result is not unexpected: an ab

initio (3-21G) molecular orbital geometry optimization for the $[\text{H}_3\text{CF-Li}]^+$ complex demonstrated a lengthening of the C–F bond from 1.403 Å in free fluoromethane to 1.471 Å in the complex [54]. The lower plot in Fig. 6 suggests that lengthening of one C–F bond in a trifluoromethyl group may lead to a slight shortening of the remaining two C–F bonds. The activation of C–F bonds by metal atoms, metal ions, and metal complexes is a current, active endeavor in both fundamental and applied chemistry [49,55,56], but statistically significant lengthening of an aliphatic C–F bond upon coordination to a metal center had not been observed before

this work [34,57]. Note that an example of lengthening of an aromatic C–F bond by coordination to zirconium(IV) has been reported [58]. Note also that lengthening of the C–F(Li) bonds in $\text{LiAl}(\text{HFPP})_4$ could not have been observed without very high quality diffraction data. It is hoped that the correlations suggested by the plots in Fig. 6 will be more fully tested experimentally, and analyzed theoretically, as additional, very precise structures of compounds containing C–F–M linkages become available in the future.

Finally, note that the four Li–F(C) bonds allow the $\text{Al}(\text{HFPP})_4^-$ anion to fully encapsulate

Table 5
Bond lengths (Å) and angles (°) for $\text{LiAl}(\text{OC}(\text{Ph})(\text{CF}_3)_2)_4$

Li–O(2)	1.966(8)	Li–O(1)	1.978(8)
Li–F(1)	1.984(9)	Li–F(10)	2.082(9)
Li–F(7)	2.098(11)	Li–F(4)	2.354(10)
Li–C(2)	2.693(8)	Li–Al	2.739(8)
Li–C(1)	2.745(8)	O(1)–C(1)	1.385(4)
O(1)–Al	1.773(2)	O(2)–C(2)	1.380(4)
O(2)–Al	1.755(3)	O(3)–C(3)	1.366(4)
O(3)–Al	1.687(3)	O(4)–C(4)	1.386(4)
O(4)–Al	1.706(3)	C(1)–C(13)	1.518(5)
C(1)–C(6)	1.534(6)	C(1)–C(5)	1.549(6)
C(2)–C(19)	1.537(5)	C(2)–C(7)	1.536(6)
C(2)–C(8)	1.555(6)	C(3)–C(9)	1.531(6)
C(3)–C(25)	1.551(5)	C(3)–C(10)	1.546(6)
C(4)–C(31)	1.527(5)	C(4)–C(12)	1.541(5)
C(4)–C(11)	1.536(5)	C(5)–F(3)	1.308(5)
C(5)–F(2)	1.335(4)	C(5)–F(1)	1.376(5)
C(6)–F(5)	1.326(5)	C(6)–F(6)	1.338(4)
C(6)–F(4)	1.341(5)	C(7)–F(8)	1.322(5)
C(7)–F(9)	1.325(5)	C(7)–F(7)	1.361(5)
C(8)–F(11)	1.298(5)	C(8)–F(12)	1.313(5)
C(8)–F(10)	1.384(5)	C(9)–F(13)	1.337(5)
C(9)–F(14)	1.338(5)	C(9)–F(15)	1.342(5)
C(10)–F(16)	1.330(4)	C(10)–F(18)	1.333(4)
C(10)–F(17)	1.339(5)	C(11)–F(19)	1.329(4)
C(11)–F(20)	1.336(4)	C(11)–F(21)	1.343(4)
C(12)–F(23)	1.328(5)	C(12)–F(22)	1.332(4)
C(12)–F(24)	1.333(5)	C(13)–C(18)	1.386(5)
C(13)–C(14)	1.391(5)	C(14)–C(15)	1.367(6)
C(15)–C(16)	1.365(6)	C(16)–C(17)	1.354(6)
C(17)–C(18)	1.371(6)	C(19)–C(20)	1.372(5)
C(19)–C(24)	1.377(5)	C(20)–C(21)	1.369(6)
C(21)–C(22)	1.372(6)	C(22)–C(23)	1.371(7)
C(23)–C(24)	1.384(6)	C(25)–C(30)	1.377(5)
C(25)–C(26)	1.397(5)	C(26)–C(27)	1.393(6)
C(27)–C(28)	1.351(6)	C(28)–C(29)	1.389(6)
C(29)–C(30)	1.390(5)	C(31)–C(32)	1.384(6)
C(31)–C(36)	1.397(6)	C(32)–C(33)	1.393(6)
C(33)–C(34)	1.358(7)	C(34)–C(35)	1.374(7)
C(35)–C(36)	1.362(6)		

Table 5 (continued)

O(2)-Li-O(1)	79.9(3)	O(2)-Li-F(1)	149.8(6)
O(1)-Li-F(1)	80.2(3)	O(2)-Li-F(10)	79.1(3)
O(1)-Li-F(10)	134.7(6)	F(1)-Li-F(10)	99.4(5)
O(2)-Li-F(7)	80.2(3)	O(1)-Li-F(7)	135.6(6)
F(1)-Li-F(7)	129.5(4)	F(10)-Li-F(7)	78.8(3)
O(2)-Li-F(4)	120.3(5)	O(1)-Li-F(4)	75.4(3)
F(1)-Li-F(4)	75.7(3)	F(10)-Li-F(4)	149.1(4)
F(7)-Li-F(4)	81.2(4)	O(2)-Li-C(2)	29.5(2)
O(1)-Li-C(2)	109.4(3)	F(1)-Li-C(2)	156.8(5)
F(10)-Li-C(2)	58.5(2)	F(7)-Li-C(2)	57.9(2)
F(4)-Li-C(2)	126.6(5)	O(2)-Li-Al	39.7(2)
O(1)-Li-Al	40.2(2)	F(1)-Li-Al	117.4(4)
F(10)-Li-Al	109.7(3)	F(7)-Li-Al	110.2(4)
F(4)-Li-Al	99.2(3)	C(2)-Li-Al	69.2(2)
O(2)-Li-C(1)	107.7(3)	O(1)-Li-C(1)	28.67(14)
F(1)-Li-C(1)	58.3(2)	F(10)-Li-C(1)	147.2(6)
F(7)-Li-C(1)	133.7(5)	F(4)-Li-C(1)	54.9(2)
C(2)-Li-C(1)	136.7(3)	Al-Li-C(1)	68.2(2)
C(1)-O(1)-Al	153.5(2)	C(1)-O(1)-Li	108.1(3)
Al-O(1)-Li	93.7(2)	C(2)-O(2)-Al	159.3(2)
C(2)-O(2)-Li	105.9(3)	Al-O(2)-Li	94.6(3)
C(3)-O(3)-Al	168.1(2)	C(4)-O(4)-Al	151.5(2)
O(3)-Al-O(4)	105.42(14)	O(3)-Al-O(2)	114.77(14)
O(4)-Al-O(2)	116.72(14)	O(3)-Al-O(1)	115.78(13)
O(4)-Al-O(1)	112.49(13)	O(2)-Al-O(1)	91.78(12)
O(3)-Al-Li	127.2(3)	O(4)-Al-Li	127.4(3)
O(2)-Al-Li	45.7(2)	O(1)-Al-Li	46.1(2)
O(1)-C(1)-C(13)	116.0(3)	O(1)-C(1)-C(6)	105.5(3)
C(13)-C(1)-C(6)	110.8(3)	O(1)-C(1)-C(5)	104.3(3)
C(13)-C(1)-C(5)	109.9(3)	C(6)-C(1)-C(5)	109.9(3)
O(1)-C(1)-Li	43.2(2)	C(13)-C(1)-Li	158.5(3)
C(6)-C(1)-Li	84.5(3)	C(5)-C(1)-Li	76.8(3)
O(2)-C(2)-C(19)	116.1(3)	O(2)-C(2)-C(7)	105.3(3)
C(19)-C(2)-C(7)	109.9(3)	O(2)-C(2)-C(8)	105.7(3)
C(19)-C(2)-C(8)	110.3(3)	C(7)-C(2)-C(8)	109.4(4)
O(2)-C(2)-Li	44.6(2)	C(19)-C(2)-Li	160.6(3)
C(7)-C(2)-Li	79.7(3)	C(8)-C(2)-Li	80.7(3)
O(3)-C(3)-C(9)	107.1(3)	O(3)-C(3)-C(25)	113.4(3)
C(9)-C(3)-C(25)	111.6(3)	O(3)-C(3)-C(10)	107.1(3)
C(9)-C(3)-C(10)	109.8(4)	C(25)-C(3)-C(10)	107.7(3)
O(4)-C(4)-C(31)	111.5(3)	O(4)-C(4)-C(12)	106.1(3)
C(31)-C(4)-C(12)	109.7(3)	O(4)-C(4)-C(11)	108.0(3)
C(31)-C(4)-C(11)	110.1(3)	C(12)-C(4)-C(11)	111.4(3)
F(3)-C(5)-F(2)	108.3(3)	F(3)-C(5)-F(1)	106.5(3)
F(2)-C(5)-F(1)	104.8(3)	F(3)-C(5)-C(1)	112.7(3)
F(2)-C(5)-C(1)	114.0(3)	F(1)-C(5)-C(1)	109.9(3)
F(5)-C(6)-F(6)	106.2(3)	F(5)-C(6)-F(4)	106.9(4)
F(6)-C(6)-F(4)	107.2(3)	F(5)-C(6)-C(1)	110.4(3)
F(6)-C(6)-C(1)	114.5(3)	F(4)-C(6)-C(1)	111.3(3)
F(8)-C(7)-F(9)	108.2(4)	F(8)-C(7)-F(7)	106.5(4)
F(9)-C(7)-F(7)	106.4(4)	F(8)-C(7)-C(2)	115.0(3)
F(9)-C(7)-C(2)	110.2(4)	F(7)-C(7)-C(2)	110.1(4)

the Li⁺ ion, making LiAl(HFPP)₄ soluble in aliphatic as well as aromatic hydrocarbons. The stabilizing effect of the Li–F(C) bonds, coupled with their presumed lability, renders the Li⁺ ion

in LiAl(HFPP)₄ an effective Lewis acid catalyst in toluene solution for the formation of carbon–carbon bonds via 1,4-conjugate addition reactions [13]. These observations underscore an

Table 5 (continued)

F(11)-C(8)-F(12)	108.7(4)	F(11)-C(8)-F(10)	106.5(3)
F(12)-C(8)-F(10)	105.0(4)	F(11)-C(8)-C(2)	115.9(4)
F(12)-C(8)-C(2)	111.1(4)	F(10)-C(8)-C(2)	109.0(3)
F(13)-C(9)-F(14)	106.1(4)	F(13)-C(9)-F(15)	107.3(4)
F(14)-C(9)-F(15)	105.9(4)	F(13)-C(9)-C(3)	111.2(4)
F(14)-C(9)-C(3)	111.8(4)	F(15)-C(9)-C(3)	114.0(4)
F(16)-C(10)-F(18)	107.4(3)	F(16)-C(10)-F(17)	106.3(3)
F(18)-C(10)-F(17)	107.3(4)	F(16)-C(10)-C(3)	112.1(4)
F(18)-C(10)-C(3)	113.3(4)	F(17)-C(10)-C(3)	110.1(3)
F(19)-C(11)-F(20)	107.2(3)	F(19)-C(11)-F(21)	106.6(3)
F(20)-C(11)-F(21)	106.6(3)	F(19)-C(11)-C(4)	110.4(3)
F(20)-C(11)-C(4)	113.7(3)	F(21)-C(11)-C(4)	111.9(3)
F(23)-C(12)-F(22)	107.4(3)	F(23)-C(12)-F(24)	107.2(3)
F(22)-C(12)-F(24)	105.7(3)	F(23)-C(12)-C(4)	110.3(3)
F(22)-C(12)-C(4)	113.7(3)	F(24)-C(12)-C(4)	112.2(3)
C(18)-C(13)-C(14)	116.6(4)	C(18)-C(13)-C(1)	122.2(4)
C(14)-C(13)-C(1)	121.2(3)	C(15)-C(14)-C(13)	121.5(4)
C(16)-C(15)-C(14)	120.5(4)	C(17)-C(16)-C(15)	119.2(5)
C(16)-C(17)-C(18)	121.0(4)	C(17)-C(18)-C(13)	121.2(4)
C(20)-C(19)-C(24)	118.5(4)	C(20)-C(19)-C(2)	120.5(4)
C(24)-C(19)-C(2)	120.9(4)	C(21)-C(20)-C(19)	121.1(4)
C(20)-C(21)-C(22)	120.4(5)	C(23)-C(22)-C(21)	119.3(4)
C(22)-C(23)-C(24)	120.0(5)	C(19)-C(24)-C(23)	120.6(4)
C(30)-C(25)-C(26)	118.7(4)	C(30)-C(25)-C(3)	118.4(3)
C(26)-C(25)-C(3)	122.8(4)	C(27)-C(26)-C(25)	119.3(4)
C(28)-C(27)-C(26)	121.8(4)	C(27)-C(28)-C(29)	119.3(4)
C(28)-C(29)-C(30)	119.8(4)	C(25)-C(30)-C(29)	121.1(4)
C(32)-C(31)-C(36)	117.9(4)	C(32)-C(31)-C(4)	120.2(4)
C(36)-C(31)-C(4)	121.9(4)	C(31)-C(32)-C(33)	120.5(5)
C(34)-C(33)-C(32)	119.8(5)	C(33)-C(34)-C(35)	120.5(5)
C(36)-C(35)-C(34)	120.1(5)	C(35)-C(36)-C(31)	121.0(5)
C(5)-F(1)-Li	113.4(3)	C(6)-F(4)-Li	106.0(3)
C(7)-F(7)-Li	109.3(3)	C(8)-F(10)-Li	111.0(3)

important principle for the design of effective weakly coordinating anions [1,2,34–36]: multiple contacts with weakly coordinating carbon–fluorine bonds may be better than multiple contacts with even more weakly coordinating carbon–hydrogen bonds. An effective weakly coordinating anion should coordinate strongly enough to the cation, and should provide enough donor atoms, to prevent extensive bridging with more strongly coordinating moieties in neighboring molecules (or ion pairs), because extensive bridging invariably leads to poor solubility in low-dielectric, low-donor-number [59,60] solvents as well as to reduced cation Lewis acidity. For example, the Li^+ ion in the unfluorinated salt $\text{LiNb}(\text{OEt})_6$ is bonded to only four ethoxide oxygen atoms from two adjacent $\text{Nb}(\text{OEt})_6^-$ an-

ions, forming a tetrahedral LiO_4 core [61]. Not surprisingly, $\text{LiNb}(\text{OEt})_6$ is not soluble in aromatic hydrocarbon solvents, whereas $\text{LiNb}(\text{HFIP})_6$ is [35].

Fig. 3 clearly shows that the aluminate anions in $\text{TlAl}(\text{HFTB})_4$ and $\text{TlAl}(\text{HFIP})_4$ coordinate to their primary Tl^+ ion in hexadentate fashion but do not fully encapsulate the very large Tl^+ ion (for comparison, the six-coordinate ionic radii of Li^+ and Tl^+ are 0.76 and 1.64 Å, respectively [62]). Instead, the two oxygen and four fluorine atoms that comprise the chelating O_2F_4 donor set are all found in one hemisphere of the coordination sphere of the Tl^+ ion. One way to better appreciate the difference between the TlO_2F_4 and LiO_2F_4 coordination units is by determining the perpendicular distance between

the metal ion and the least-squares plane formed by F1, F4, F7, and F10. The Li^+ ion in $\text{LiAl}(\text{HFPP})_4$ is 0.70 Å ‘below’ the F_4 plane (i.e., on the same side of the F_4 plane as O1 and O2), while the Ti^+ ions in $\text{TiAl}(\text{HFTB})_4$ and $\text{TiAl}(\text{HFIP})_4$ are 0.37 and 0.75 Å ‘above’ their respective F_4 planes. These displacement distances as well as other pertinent results are listed in Table 18. The C–F(Ti) bonds were not

longer (to within $\pm 3\sigma$) than the other C–F bonds in either $\text{TiAl}(\text{HFTB})_4$ or $\text{TiAl}(\text{HFIP})_4$.

4.2. Bond–valence analysis of $\text{LiAl}(\text{HFPP})_4$, $\text{TiAl}(\text{HFTB})_4$, and $\text{TiAl}(\text{HFIP})_4$

The advent of larger and more-weakly-coordinating anions, which has allowed the isolation

Table 6

Anisotropic displacement parameters ($\text{Å}^2 \times 10^3$) for $\text{LiAl}(\text{OC}(\text{Ph})(\text{CF}_3)_2)_4$

	U11	U22	U33	U23	U13	U12
Li	57 (5)	118 (8)	26 (4)	-18 (5)	-7 (4)	51 (6)
O(1)	17 (1)	32 (2)	26 (1)	-1 (1)	-1 (1)	5 (1)
O(2)	36 (2)	45 (2)	26 (2)	-6 (1)	9 (1)	11 (1)
O(3)	26 (2)	19 (1)	43 (2)	2 (1)	12 (1)	0 (1)
O(4)	19 (1)	28 (2)	48 (2)	5 (1)	15 (1)	-1 (1)
Al	18 (1)	24 (1)	25 (1)	0 (1)	7 (1)	1 (1)
C(1)	24 (2)	33 (2)	30 (2)	-1 (2)	9 (2)	3 (2)
C(2)	31 (2)	35 (2)	24 (2)	-4 (2)	9 (2)	4 (2)
C(3)	25 (2)	20 (2)	37 (2)	2 (2)	10 (2)	3 (2)
C(4)	25 (2)	30 (2)	28 (2)	2 (2)	11 (2)	-4 (2)
C(5)	30 (2)	42 (3)	38 (3)	-3 (2)	2 (2)	13 (2)
C(6)	24 (2)	50 (3)	33 (2)	-1 (2)	6 (2)	4 (2)
C(7)	32 (3)	57 (3)	42 (3)	-12 (2)	11 (2)	-5 (2)
C(8)	44 (3)	40 (3)	32 (3)	-3 (2)	13 (2)	7 (2)
C(9)	41 (3)	40 (3)	61 (4)	13 (3)	18 (3)	1 (2)
C(10)	33 (3)	25 (2)	51 (3)	-6 (2)	7 (2)	1 (2)
C(11)	33 (2)	33 (2)	38 (2)	5 (2)	22 (2)	-3 (2)
C(12)	30 (2)	44 (3)	35 (3)	-4 (2)	15 (2)	-8 (2)
C(13)	20 (2)	34 (2)	27 (2)	3 (2)	5 (2)	5 (2)
C(14)	32 (3)	74 (3)	32 (3)	-6 (2)	5 (2)	20 (2)
C(15)	41 (3)	105 (5)	38 (3)	-16 (3)	12 (2)	29 (3)
C(16)	44 (3)	88 (4)	34 (3)	0 (3)	15 (2)	7 (3)
C(17)	53 (3)	108 (5)	32 (3)	9 (3)	9 (2)	37 (3)
C(18)	36 (3)	87 (4)	38 (3)	2 (3)	9 (2)	26 (3)
C(19)	27 (2)	33 (2)	34 (2)	0 (2)	11 (2)	1 (2)
C(20)	36 (3)	60 (3)	30 (2)	4 (2)	13 (2)	10 (2)
C(21)	44 (3)	80 (4)	47 (3)	10 (3)	16 (3)	29 (3)
C(22)	49 (3)	79 (4)	45 (3)	15 (3)	9 (3)	28 (3)
C(23)	66 (4)	84 (4)	30 (3)	1 (3)	1 (3)	31 (3)
C(24)	50 (3)	63 (3)	31 (3)	-7 (2)	7 (2)	17 (3)
C(25)	30 (2)	29 (2)	23 (2)	-4 (2)	11 (2)	4 (2)
C(26)	45 (3)	29 (2)	31 (2)	-2 (2)	5 (2)	7 (2)
C(27)	54 (3)	43 (3)	39 (3)	0 (2)	15 (2)	19 (3)
C(28)	35 (3)	55 (3)	41 (3)	-2 (2)	7 (2)	14 (2)
C(29)	28 (2)	48 (3)	45 (3)	-2 (2)	15 (2)	7 (2)
C(30)	29 (2)	35 (2)	36 (2)	0 (2)	12 (2)	8 (2)
C(31)	24 (2)	47 (3)	28 (2)	8 (2)	9 (2)	9 (2)
C(32)	30 (2)	50 (3)	40 (3)	-9 (2)	5 (2)	5 (2)
C(33)	45 (3)	81 (4)	41 (3)	-14 (3)	5 (3)	24 (3)
C(34)	52 (3)	123 (6)	35 (3)	5 (3)	20 (3)	38 (4)
C(35)	44 (3)	99 (5)	45 (3)	19 (3)	27 (3)	19 (3)
C(36)	33 (2)	62 (3)	49 (3)	14 (3)	25 (2)	10 (2)

Table 6 (continued)

F(1)	55(2)	51(2)	47(2)	-12(1)	5(1)	25(1)
F(2)	32(1)	55(2)	53(2)	-1(1)	1(1)	24(1)
F(3)	49(2)	35(2)	76(2)	11(1)	21(2)	3(1)
F(4)	44(2)	86(2)	45(2)	-12(2)	25(1)	-7(2)
F(5)	43(2)	43(2)	66(2)	4(1)	21(1)	-10(1)
F(6)	21(1)	73(2)	55(2)	0(1)	4(1)	-7(1)
F(7)	30(1)	99(2)	51(2)	-8(2)	13(1)	8(2)
F(8)	50(2)	100(2)	52(2)	-2(2)	32(1)	-5(2)
F(9)	55(2)	60(2)	111(3)	-12(2)	46(2)	-21(2)
F(10)	74(2)	52(2)	43(2)	3(1)	17(1)	32(2)
F(11)	70(2)	51(2)	39(2)	-13(1)	26(1)	8(1)
F(12)	66(2)	43(2)	71(2)	-4(1)	37(2)	-9(1)
F(13)	59(2)	71(2)	52(2)	17(2)	32(2)	10(2)
F(14)	36(2)	60(2)	86(2)	16(2)	36(2)	3(1)
F(15)	65(2)	34(2)	110(2)	11(2)	44(2)	-8(1)
F(16)	29(1)	58(2)	54(2)	-6(1)	-3(1)	0(1)
F(17)	47(2)	60(2)	37(2)	-5(1)	16(1)	1(1)
F(18)	60(2)	32(2)	60(2)	-16(1)	6(1)	5(1)
F(19)	37(1)	43(1)	38(1)	8(1)	11(1)	9(1)
F(20)	52(2)	30(1)	66(2)	5(1)	33(1)	-8(1)
F(21)	45(1)	34(1)	42(1)	1(1)	25(1)	2(1)
F(22)	36(1)	66(2)	48(2)	-3(1)	10(1)	-29(1)
F(23)	29(1)	56(2)	56(2)	6(1)	2(1)	11(1)
F(24)	40(2)	81(2)	35(1)	-1(1)	13(1)	-5(1)

The anisotropic displacement factor exponent takes the form: $-2\pi^2((ha^*)^2U_{11} + \dots + 2hka^*b^*U_{12})$.

Table 7

Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{LiAl}(\text{OC}(\text{Ph})(\text{CF}_3)_2)_4$

	x	y	z	U(eq)
H(14A)	1604(1)	2925(5)	1882(2)	59
H(15A)	1601(1)	3586(5)	3024(3)	76
H(16A)	2035(1)	2947(5)	4190(3)	67
H(17A)	2508(1)	1862(5)	4200(3)	81
H(18A)	2529(1)	1244(5)	3066(3)	67
H(20A)	882(1)	3366(4)	-1030(2)	51
H(21A)	397(1)	4441(5)	-1868(3)	69
H(22A)	201(1)	4181(5)	-3190(3)	73
H(23A)	509(1)	2894(5)	-3666(3)	80
H(24A)	1006(1)	1843(4)	-2819(2)	61
H(26A)	1001(1)	7534(4)	-452(2)	46
H(27A)	410(1)	8034(5)	-946(2)	56
H(28A)	10(1)	6637(5)	-882(2)	56
H(29A)	199(1)	4692(4)	-272(2)	48
H(30A)	789(1)	4175(4)	240(2)	40
H(32A)	977(1)	3223(4)	1521(2)	52
H(33A)	806(1)	3774(5)	2495(3)	72
H(34A)	436(1)	2481(7)	2771(3)	83
H(35A)	237(1)	618(6)	2100(3)	72
H(36A)	408(1)	43(5)	1149(3)	54

of metal complexes with extremely weak metal–ligand (or metal–solvent) bonds such as $\text{Ag}^+(\text{CH}_2\text{Cl}_2)$ [63], Ag^+CO [64], $\text{Na}^+(\eta^6\text{-C}_6\text{H}_6)$ [34], (porphyrin) $\text{Fe}^+(\eta^2\text{-C}_6\text{H}_4\text{R}_2)$ [65],

and $\text{Tl}^+(\eta^6\text{-C}_6\text{H}_3\text{R}_3)$ [66,67], has also raised a number of interesting issues. As metal–ligand bonds become weaker and weaker, the distinction between ‘coordination’ and ‘solvation’, for

Table 8

Crystal data and structure refinement for $\text{TlAl}(\text{OC}(\text{CH}_3)(\text{CF}_3)_2)_4$

Identification code	shs66
Empirical formula	$\text{C}_{16}\text{H}_{12}\text{AlF}_{24}\text{O}_4\text{Tl}$
Formula weight	955.61
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$\text{P}2_1/\text{c}$
Unit cell dimensions	$a = 12.650(3)$ Å $\alpha = 90^\circ$ $b = 9.970(2)$ Å $\beta = 94.00(3)^\circ$ $c = 21.237(4)$ Å $\gamma = 90^\circ$
Volume, Z	$2671.9(10)$ Å ³ , 4
Density (calculated)	2.376 Mg/m ³
Absorption coefficient	6.271
F(000)	1800
Crystal size	0.24 x 0.14 x 0.02 mm
θ range for data collection	2.26 to 25.03°
Limiting indices	$0 \leq h \leq 15$, $0 \leq k \leq 11$, $-25 \leq l \leq 25$
Reflections collected	4946
Independent reflections	4707 ($R_{\text{int}} = 0.0860$)
Absorption correction	Semi-empirical from psi-scans
Max. and min. transmission	0.714 and 0.498
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4706 / 0 / 411
Goodness-of-fit on F^2	1.060
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0734$, $wR2 = 0.1422$
R indices (all data)	$R1 = 0.1426$, $wR2 = 0.1759$
Extinction coefficient	0.0
Largest diff. peak and hole	2.164 and -2.287 eÅ ⁻³

example, becomes even more blurred than usual [3,65]. The concept of ‘primary’ and ‘secondary’ chemical bonds has been used with

some success, especially for nonmetallic elements [53], but it is perhaps not well suited for metallic elements. This is because the concept

Table 9

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{TiAl}(\text{OC}(\text{CH}_3)(\text{CF}_3)_2)_4$

	x	y	z	U(eq)
Ti1	9274(1)	937(1)	2253(1)	32(1)
Al	7557(3)	3539(4)	1595(2)	20(1)
O(1)	8651(7)	2673(10)	1304(4)	21(2)
O(2)	7678(7)	2735(10)	2342(4)	21(2)
O(3)	6366(7)	3252(10)	1192(5)	24(2)
O(4)	7789(8)	5221(10)	1639(5)	26(2)
C(1)	9282(12)	2797(15)	805(7)	23(3)
C(2)	10343(15)	3422(19)	1067(8)	38(5)
C(3)	9438(14)	1438(17)	547(8)	38(4)
C(4)	8822(14)	3719(15)	278(7)	36(4)
C(5)	7273(12)	2971(17)	2926(7)	30(4)
C(6)	6913(13)	1573(17)	3173(7)	29(4)
C(7)	8169(14)	3494(18)	3376(8)	36(4)
C(8)	6341(11)	3916(17)	2908(8)	34(4)
C(9)	5669(12)	2337(15)	949(7)	27(4)
C(10)	4594(15)	2612(19)	1181(9)	45(5)
C(11)	5627(14)	2493(18)	225(8)	35(4)
C(12)	6011(13)	906(16)	1132(8)	39(4)
C(13)	7330(11)	6489(15)	1511(7)	25(4)
C(14)	7754(15)	7417(17)	2036(9)	44(5)
C(15)	7697(15)	6963(17)	893(9)	42(5)
C(16)	6142(13)	6475(18)	1483(9)	45(5)
F(1)	10788(8)	2695(12)	1528(5)	58(3)
F(2)	10205(8)	4622(11)	1313(5)	53(3)
F(3)	11044(7)	3523(10)	642(5)	45(3)
F(4)	9850(9)	555(10)	966(4)	50(3)
F(5)	10062(9)	1432(10)	55(5)	52(3)
F(6)	8534(8)	923(10)	313(4)	44(2)
F(7)	7664(8)	648(10)	3185(5)	50(3)
F(8)	6135(8)	1098(9)	2780(4)	47(3)
F(9)	6545(9)	1639(11)	3731(4)	55(3)
F(10)	9004(8)	2694(12)	3425(5)	56(3)
F(11)	8513(8)	4668(11)	3149(5)	55(3)
F(12)	7898(9)	3721(12)	3951(4)	59(3)
F(13)	3832(8)	1761(12)	995(6)	64(3)
F(14)	4253(9)	3817(12)	1035(7)	76(4)
F(15)	4633(8)	2536(14)	1807(5)	74(4)
F(16)	4868(10)	1670(11)	-51(5)	64(3)
F(17)	5391(11)	3680(11)	42(6)	75(4)
F(18)	6504(9)	2085(14)	0(5)	68(3)
F(19)	8817(7)	7523(10)	2063(5)	44(3)
F(20)	7363(10)	8660(10)	1969(6)	71(4)
F(21)	7428(8)	6986(10)	2589(4)	49(3)
F(22)	7280(9)	6212(11)	400(5)	56(3)
F(23)	7397(10)	8253(11)	753(5)	69(4)
F(24)	8762(8)	6954(10)	866(4)	48(3)

$U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

of a van der Waals radius is more meaningful for nonmetallic elements than for metallic elements, since metal atoms or ions are usually shielded from nonbonded contacts [68].

Nevertheless, van der Waals radii for some metals have been proposed, and for lithium and thallium they are 1.82 and 1.96 Å, respectively [68]. The recommended values for oxygen and

Table 10
Bond lengths (Å) and angles (°) for TlAl(OC(CH₃)(CF₃)₂)₄

Tl-O(2)	2.717(9)	Tl-O(1)	2.731(9)
Tl-F(4)	2.903(9)	Tl-F(7)	2.952(10)
Tl-F(10)	3.081(11)	Tl-F(1)	3.087(10)
Tl-F(19)#1	3.154(10)	Tl-F(11)#1	3.240(10)
Tl-F(2)#1	3.339(10)	Tl-F(20)#2	3.341(12)
Tl-F(19)#2	3.471(10)	Tl-C(1)	3.591(14)
Tl-Al	3.603(4)	Tl-C(5)	3.61(2)
Tl-C(3)	3.68(2)	Tl-C(6)	3.74(2)
Tl-F(1)#1	4.145(12)	Tl-F(6)	4.162(9)
Al-O(3)	1.704(10)	Al-O(4)	1.704(11)
Al-O(2)	1.775(10)	Al-O(1)	1.778(10)
O(1)-C(1)	1.38(2)	O(1)-C(3)	2.31(2)
O(1)-C(2)	2.35(2)	O(1)-C(4)	2.44(2)
O(1)-O(2)	2.599(12)	O(1)-F(1)	2.712(13)
O(1)-F(4)	2.725(13)	O(2)-C(5)	1.39(2)
O(2)-C(7)	2.36(2)	O(2)-C(6)	2.37(2)
O(2)-C(8)	2.44(2)	O(2)-F(11)	2.742(13)
O(3)-C(9)	1.35(2)	O(3)-C(11)	2.32(2)
O(3)-C(10)	2.33(2)	O(3)-C(12)	2.38(2)
O(3)-F(17)	2.692(15)	O(3)-F(15)	2.724(14)
O(3)-F(14)	2.730(14)	O(4)-C(13)	1.41(2)
O(4)-C(14)	2.35(2)	O(4)-C(15)	2.35(2)
O(4)-C(16)	2.43(2)	O(4)-F(24)	2.734(14)
O(4)-F(21)	2.740(13)	O(4)-F(19)	2.757(13)
C(1)-C(3)	1.48(2)	C(1)-C(4)	1.53(2)
C(1)-C(2)	1.55(2)	C(1)-F(6)	2.31(2)
C(1)-F(5)	2.36(2)	C(1)-F(1)	2.36(2)
C(1)-F(4)	2.36(2)	C(1)-F(2)	2.38(2)
C(1)-F(3)	2.39(2)	C(2)-F(1)	1.31(2)
C(2)-F(3)	1.31(2)	C(2)-F(2)	1.32(2)
C(3)-F(6)	1.32(2)	C(3)-F(4)	1.33(2)
C(3)-F(5)	1.35(2)	C(5)-C(8)	1.51(2)
C(5)-C(7)	1.52(2)	C(5)-C(6)	1.57(2)
C(5)-F(11)	2.33(2)	C(5)-F(8)	2.36(2)
C(5)-F(10)	2.38(2)	C(5)-F(12)	2.38(2)
C(5)-F(9)	2.40(2)	C(5)-F(7)	2.42(2)
C(6)-F(9)	1.30(2)	C(6)-F(7)	1.32(2)
C(6)-F(8)	1.33(2)	C(7)-F(12)	1.31(2)
C(7)-F(10)	1.32(2)	C(7)-F(11)	1.35(2)
C(9)-C(10)	1.50(2)	C(9)-C(12)	1.53(2)
C(9)-C(11)	1.54(2)	C(9)-F(15)	2.33(2)
C(9)-F(14)	2.34(2)	C(9)-F(17)	2.35(2)
C(9)-F(18)	2.35(2)	C(9)-F(16)	2.38(2)
C(9)-F(13)	2.40(2)	C(10)-F(14)	1.31(2)
C(10)-F(13)	1.32(2)	C(10)-F(15)	1.33(2)
C(11)-F(17)	1.27(2)	C(11)-F(18)	1.30(2)
C(11)-F(16)	1.36(2)	C(13)-C(15)	1.50(2)
C(13)-C(16)	1.50(2)	C(13)-C(14)	1.52(2)
C(13)-F(21)	2.34(2)	C(13)-F(22)	2.37(2)
C(13)-F(20)	2.37(2)	C(13)-F(19)	2.38(2)
C(13)-F(23)	2.39(2)	C(13)-F(24)	2.39(2)
C(14)-F(20)	1.34(2)	C(14)-F(21)	1.34(2)
C(14)-F(19)	1.35(2)	C(15)-F(24)	1.35(2)
C(15)-F(22)	1.36(2)	C(15)-F(23)	1.37(2)

Table 10 (continued)

F(1)-F(2)	2.10(2)	F(1)-F(3)	2.100(14)
F(1)-F(4)	2.68(2)	F(1)-Tl#3	4.145(12)
F(2)-F(3)	2.137(14)	F(2)-Tl#3	3.339(10)
F(3)-F(5)	2.688(15)	F(4)-F(6)	2.123(13)
F(4)-F(5)	2.156(14)	F(4)-F(11)#1	2.839(13)
F(5)-F(6)	2.107(15)	F(5)-F(5)#4	2.87(2)
F(6)-F(18)	2.85(2)	F(7)-F(8)	2.109(14)
F(7)-F(9)	2.133(14)	F(7)-F(10)	2.678(15)
F(8)-F(9)	2.119(14)	F(9)-F(12)	2.711(15)
F(10)-F(12)	2.12(2)	F(10)-F(11)	2.13(2)
F(11)-F(12)	2.141(14)	F(11)-F(4)#3	2.839(13)
F(11)-Tl#3	3.240(10)	F(13)-F(15)	2.09(2)
F(13)-F(14)	2.12(2)	F(13)-F(16)	2.66(2)
F(14)-F(15)	2.11(2)	F(14)-F(17)	2.64(2)
F(16)-F(18)	2.11(2)	F(16)-F(17)	2.12(2)
F(17)-F(18)	2.13(2)	F(17)-F(17)#5	2.81(2)
F(19)-F(20)	2.158(15)	F(19)-F(21)	2.213(14)
F(19)-F(24)	2.601(13)	F(19)-Tl#3	3.154(10)
F(19)-Tl#6	3.471(10)	F(20)-F(21)	2.12(2)
F(20)-F(23)	2.62(2)	F(20)-Tl#6	3.341(12)
F(22)-F(23)	2.17(2)	F(22)-F(24)	2.187(14)
F(23)-F(24)	2.158(15)		
O(2)-Tl-O(1)	57.0(3)	O(2)-Tl-F(4)	112.8(3)
O(1)-Tl-F(4)	57.8(3)	O(2)-Tl-F(7)	57.8(3)
O(1)-Tl-F(7)	112.3(3)	F(4)-Tl-F(7)	148.1(3)
O(2)-Tl-F(10)	56.2(3)	O(1)-Tl-F(10)	101.1(3)
F(4)-Tl-F(10)	152.2(3)	F(7)-Tl-F(10)	52.7(3)
O(2)-Tl-F(1)	98.6(3)	O(1)-Tl-F(1)	55.2(3)
F(4)-Tl-F(1)	53.1(3)	F(7)-Tl-F(1)	150.6(3)
F(10)-Tl-F(1)	100.8(3)	O(2)-Tl-F(19)#1	100.7(3)
O(1)-Tl-F(19)#1	101.2(3)	F(4)-Tl-F(19)#1	105.4(3)
F(7)-Tl-F(19)#1	106.4(3)	F(10)-Tl-F(19)#1	57.9(3)
F(1)-Tl-F(19)#1	57.5(2)	O(2)-Tl-F(11)#1	159.3(3)
O(1)-Tl-F(11)#1	105.2(3)	F(4)-Tl-F(11)#1	54.7(3)
F(7)-Tl-F(11)#1	142.0(3)	F(10)-Tl-F(11)#1	125.6(3)
F(1)-Tl-F(11)#1	60.8(3)	F(19)#1-Tl-F(11)#1	70.7(3)
O(2)-Tl-F(2)#1	107.2(3)	O(1)-Tl-F(2)#1	161.9(3)
F(4)-Tl-F(2)#1	139.6(3)	F(7)-Tl-F(2)#1	56.8(3)
F(10)-Tl-F(2)#1	60.8(3)	F(1)-Tl-F(2)#1	126.0(3)
F(19)#1-Tl-F(2)#1	71.4(3)	F(11)#1-Tl-F(2)#1	88.2(2)
O(2)-Tl-F(20)#2	85.9(3)	O(1)-Tl-F(20)#2	97.4(3)
F(4)-Tl-F(20)#2	88.1(3)	F(7)-Tl-F(20)#2	62.0(3)
F(10)-Tl-F(20)#2	114.4(3)	F(1)-Tl-F(20)#2	139.7(3)
F(19)#1-Tl-F(20)#2	160.9(3)	F(11)#1-Tl-F(20)#2	108.4(3)
F(2)#1-Tl-F(20)#2	89.6(3)	O(2)-Tl-F(19)#2	122.5(2)
O(1)-Tl-F(19)#2	119.9(3)	F(4)-Tl-F(19)#2	79.2(3)
F(7)-Tl-F(19)#2	82.3(2)	F(10)-Tl-F(19)#2	128.6(3)
F(1)-Tl-F(19)#2	127.1(3)	F(19)#1-Tl-F(19)#2	131.4(2)
F(11)#1-Tl-F(19)#2	74.1(3)	F(2)#1-Tl-F(19)#2	75.0(3)
F(20)#2-Tl-F(19)#2	36.9(2)	O(2)-Tl-C(1)	76.4(3)
O(1)-Tl-C(1)	19.7(3)	F(4)-Tl-C(1)	41.0(3)
F(7)-Tl-C(1)	131.9(3)	F(10)-Tl-C(1)	113.9(3)
F(1)-Tl-C(1)	40.6(3)	F(19)#1-Tl-C(1)	95.0(3)
F(11)#1-Tl-C(1)	85.5(3)	F(2)#1-Tl-C(1)	166.3(3)
F(20)#2-Tl-C(1)	104.0(3)	F(19)#2-Tl-C(1)	114.6(3)
O(2)-Tl-Al	28.4(2)	O(1)-Tl-Al	28.6(2)
F(4)-Tl-Al	85.0(2)	F(7)-Tl-Al	84.5(2)

fluorine are 1.52 and 1.47 Å, respectively [68]. Therefore, the sum of van der Waals radii for lithium and fluorine is 3.29 Å, nearly 1 Å

longer than the longest Li-F(C) distance in LiAl(HFPP)₄. However, is there a way to assess the relative strengths of the Li-F1 bond, at

Table 10 (continued)

F(10) -Tl-Al	78.8(2)	F(1) -Tl-Al	77.0(2)
F(19)#1-Tl-Al	103.8(2)	F(11)#1-Tl-Al	133.4(2)
F(2)#1-Tl-Al	135.4(2)	F(20)#2-Tl-Al	90.6(2)
F(19)#2-Tl-Al	124.7(2)	C(1) -Tl-Al	48.2(2)
O(2) -Tl-C(5)	19.6(3)	O(1) -Tl-C(5)	76.2(3)
F(4) -Tl-C(5)	132.4(3)	F(7) -Tl-C(5)	41.8(3)
F(10) -Tl-C(5)	40.7(3)	F(1) -Tl-C(5)	110.8(3)
F(19)#1-Tl-C(5)	94.1(3)	F(11)#1-Tl-C(5)	164.8(3)
F(2)#1-Tl-C(5)	87.7(3)	F(20)#2-Tl-C(5)	86.3(3)
F(19)#2-Tl-C(5)	118.7(3)	C(1) -Tl-C(5)	95.3(3)
Al-Tl-C(5)	47.9(2)	O(2) -Tl-C(3)	94.1(3)
O(1) -Tl-C(3)	38.7(3)	F(4) -Tl-C(3)	19.1(3)
F(7) -Tl-C(3)	139.7(4)	F(10) -Tl-C(3)	137.3(3)
F(1) -Tl-C(3)	49.6(3)	F(19)#1-Tl-C(3)	106.9(3)
F(11)#1-Tl-C(3)	71.6(3)	F(2)#1-Tl-C(3)	158.6(3)
F(20)#2-Tl-C(3)	90.2(4)	F(19)#2-Tl-C(3)	92.2(3)
C(1) -Tl-C(3)	23.5(3)	Al-Tl-C(3)	66.0(3)
C(5) -Tl-C(3)	113.7(4)	O(2) -Tl-C(6)	39.3(3)
O(1) -Tl-C(6)	94.5(3)	F(4) -Tl-C(6)	141.0(3)
F(7) -Tl-C(6)	18.5(3)	F(10) -Tl-C(6)	49.0(3)
F(1) -Tl-C(6)	135.3(3)	F(19)#1-Tl-C(6)	106.8(3)
F(11)#1-Tl-C(6)	160.3(3)	F(2)#1-Tl-C(6)	72.8(3)
F(20)#2-Tl-C(6)	67.3(3)	F(19)#2-Tl-C(6)	95.4(3)
C(1) -Tl-C(6)	114.2(3)	Al-Tl-C(6)	66.3(3)
C(5) -Tl-C(6)	24.6(3)	C(3) -Tl-C(6)	126.4(4)
O(2) -Tl-F(1)#1	115.1(2)	O(1) -Tl-F(1)#1	159.7(2)
F(4) -Tl-F(1)#1	120.2(2)	F(7) -Tl-F(1)#1	57.4(2)
F(10) -Tl-F(1)#1	86.0(2)	F(1) -Tl-F(1)#1	142.58(14)
F(19)#1-Tl-F(1)#1	98.7(2)	F(11)#1-Tl-F(1)#1	85.1(2)
F(2)#1-Tl-F(1)#1	30.2(2)	F(20)#2-Tl-F(1)#1	62.5(2)
F(19)#2-Tl-F(1)#1	45.4(2)	C(1) -Tl-F(1)#1	159.8(3)
Al-Tl-F(1)#1	140.1(2)	C(5) -Tl-F(1)#1	98.4(3)
C(3) -Tl-F(1)#1	136.6(3)	C(6) -Tl-F(1)#1	75.8(3)
O(2) -Tl-F(6)	87.3(2)	O(1) -Tl-F(6)	40.4(2)
F(4) -Tl-F(6)	28.5(2)	F(7) -Tl-F(6)	123.0(2)
F(10) -Tl-F(6)	140.5(2)	F(1) -Tl-F(6)	67.2(2)
F(19)#1-Tl-F(6)	124.7(2)	F(11)#1-Tl-F(6)	82.9(2)
F(2)#1-Tl-F(6)	156.7(2)	F(20)#2-Tl-F(6)	73.1(3)
F(19)#2-Tl-F(6)	81.8(2)	C(1) -Tl-F(6)	33.7(3)
Al-Tl-F(6)	61.98(15)	C(5) -Tl-F(6)	106.1(3)
C(3) -Tl-F(6)	18.0(3)	C(6) -Tl-F(6)	112.7(3)
F(1)#1-Tl-F(6)	127.1(2)	O(3) -Al-O(4)	109.6(5)
O(3) -Al-O(2)	113.0(5)	O(4) -Al-O(2)	113.1(5)
O(3) -Al-O(1)	115.2(5)	O(4) -Al-O(1)	111.2(5)
O(2) -Al-O(1)	94.0(5)	O(3) -Al-Tl	124.2(4)
O(4) -Al-Tl	126.2(4)	O(2) -Al-Tl	46.8(3)
O(1) -Al-Tl	47.3(3)	C(1) -O(1) -Al	137.0(9)
C(1) -O(1) -C(3)	37.7(8)	Al-O(1) -C(3)	152.4(7)
C(1) -O(1) -C(2)	38.9(8)	Al-O(1) -C(2)	131.4(7)
C(3) -O(1) -C(2)	65.0(7)	C(1) -O(1) -C(4)	35.1(8)
Al-O(1) -C(4)	102.8(6)	C(3) -O(1) -C(4)	62.4(6)
C(2) -O(1) -C(4)	62.3(6)	C(1) -O(1) -O(2)	170.2(9)
Al-O(1) -O(2)	42.9(3)	C(3) -O(1) -O(2)	149.0(7)
C(2) -O(1) -O(2)	131.7(6)	C(4) -O(1) -O(2)	145.5(6)
C(1) -O(1) -F(1)	60.6(7)	Al-O(1) -F(1)	136.5(5)
C(3) -O(1) -F(1)	69.7(6)	C(2) -O(1) -F(1)	28.9(5)
C(4) -O(1) -F(1)	90.2(5)	O(2) -O(1) -F(1)	112.1(4)
C(1) -O(1) -F(4)	60.2(7)	Al-O(1) -F(4)	158.2(6)

1.984(9) Å, and the Li–F4 bond, at 2.354(10) Å? Are the set of four Li–F(C) bonds completely ion-dipole in nature, or is there any

incipient covalency? The sum of van der Waals radii for thallium and fluorine is 3.43 Å. What is the coordination number of the Tl⁺ ion in

Table 10 (continued)

C(3)-O(1)-F(4)	29.2(5)	C(2)-O(1)-F(4)	70.0(6)
C(4)-O(1)-F(4)	90.6(5)	O(2)-O(1)-F(4)	123.2(5)
F(1)-O(1)-F(4)	59.1(4)	C(5)-O(2)-Al	134.8(10)
C(5)-O(2)-C(7)	37.7(7)	Al-O(2)-C(7)	133.4(7)
C(5)-O(2)-C(6)	39.4(8)	Al-O(2)-C(6)	150.6(6)
C(7)-O(2)-C(6)	63.9(6)	C(5)-O(2)-C(8)	34.1(8)
Al-O(2)-C(8)	101.7(6)	C(7)-O(2)-C(8)	62.3(6)
C(6)-O(2)-C(8)	62.4(6)	C(5)-O(2)-O(1)	169.5(9)
Al-O(2)-O(1)	43.0(3)	C(7)-O(2)-O(1)	133.3(6)
C(6)-O(2)-O(1)	149.4(6)	C(8)-O(2)-O(1)	144.4(6)
C(5)-O(2)-Tl	119.6(8)	Al-O(2)-Tl	104.7(4)
C(7)-O(2)-Tl	97.3(5)	C(6)-O(2)-Tl	94.2(5)
C(8)-O(2)-Tl	153.5(5)	O(1)-O(2)-Tl	61.8(3)
C(5)-O(2)-F(11)	58.3(7)	Al-O(2)-F(11)	104.3(5)
C(7)-O(2)-F(11)	29.5(4)	C(6)-O(2)-F(11)	92.2(5)
C(8)-O(2)-F(11)	66.6(5)	O(1)-O(2)-F(11)	111.2(5)
Tl-O(2)-F(11)	104.6(4)	C(9)-O(3)-Al	147.1(10)
C(9)-O(3)-C(11)	39.4(8)	Al-O(3)-C(11)	141.8(7)
C(9)-O(3)-C(10)	37.5(8)	Al-O(3)-C(10)	150.2(7)
C(11)-O(3)-C(10)	64.8(7)	C(9)-O(3)-C(12)	36.8(8)
Al-O(3)-C(12)	110.4(6)	C(11)-O(3)-C(12)	64.5(7)
C(10)-O(3)-C(12)	63.5(7)	C(9)-O(3)-F(17)	60.8(8)
Al-O(3)-F(17)	139.6(6)	C(11)-O(3)-F(17)	28.2(5)
C(10)-O(3)-F(17)	69.8(6)	C(12)-O(3)-F(17)	92.0(5)
C(9)-O(3)-F(15)	58.6(8)	Al-O(3)-F(15)	121.1(5)
C(11)-O(3)-F(15)	92.9(6)	C(10)-O(3)-F(15)	29.2(5)
C(12)-O(3)-F(15)	67.3(6)	F(17)-O(3)-F(15)	98.2(5)
C(9)-O(3)-F(14)	58.9(8)	Al-O(3)-F(14)	148.3(6)
C(11)-O(3)-F(14)	68.2(6)	C(10)-O(3)-F(14)	28.5(5)
C(12)-O(3)-F(14)	90.9(6)	F(17)-O(3)-F(14)	58.2(5)
F(15)-O(3)-F(14)	45.4(4)	C(13)-O(4)-Al	143.6(9)
C(13)-O(4)-C(14)	38.3(8)	Al-O(4)-C(14)	158.4(8)
C(13)-O(4)-C(15)	37.5(8)	Al-O(4)-C(15)	133.7(7)
C(14)-O(4)-C(15)	63.3(7)	C(13)-O(4)-C(16)	34.4(7)
Al-O(4)-C(16)	110.8(7)	C(14)-O(4)-C(16)	62.1(6)
C(15)-O(4)-C(16)	61.7(7)	C(13)-O(4)-F(24)	61.0(7)
Al-O(4)-F(24)	132.2(6)	C(14)-O(4)-F(24)	69.3(6)
C(15)-O(4)-F(24)	29.7(5)	C(16)-O(4)-F(24)	90.6(6)
C(13)-O(4)-F(21)	58.6(8)	Al-O(4)-F(21)	129.5(6)
C(14)-O(4)-F(21)	29.3(5)	C(15)-O(4)-F(21)	91.1(6)
C(16)-O(4)-F(21)	65.5(5)	F(24)-O(4)-F(21)	98.2(4)
C(13)-O(4)-F(19)	59.7(7)	Al-O(4)-F(19)	155.8(6)
C(14)-O(4)-F(19)	29.2(5)	C(15)-O(4)-F(19)	66.8(6)
C(16)-O(4)-F(19)	89.8(6)	F(24)-O(4)-F(19)	56.5(4)
F(21)-O(4)-F(19)	47.5(3)	O(1)-C(1)-C(3)	107.6(12)
O(1)-C(1)-C(4)	113.9(12)	C(3)-C(1)-C(4)	109.4(13)
O(1)-C(1)-C(2)	107.1(11)	C(3)-C(1)-C(2)	111.6(14)
C(4)-C(1)-C(2)	107.2(13)	O(1)-C(1)-F(6)	92.0(9)
C(3)-C(1)-F(6)	32.2(8)	C(4)-C(1)-F(6)	91.8(9)
C(2)-C(1)-F(6)	143.7(11)	O(1)-C(1)-F(5)	139.5(10)
C(3)-C(1)-F(5)	31.8(8)	C(4)-C(1)-F(5)	90.4(9)
C(2)-C(1)-F(5)	94.7(10)	F(6)-C(1)-F(5)	53.6(5)
O(1)-C(1)-F(1)	88.9(8)	C(3)-C(1)-F(1)	94.5(11)
C(4)-C(1)-F(1)	138.4(11)	C(2)-C(1)-F(1)	31.2(7)
F(6)-C(1)-F(1)	123.1(7)	F(5)-C(1)-F(1)	93.3(7)
O(1)-C(1)-F(4)	89.5(8)	C(3)-C(1)-F(4)	30.8(8)
C(4)-C(1)-F(4)	140.2(10)	C(2)-C(1)-F(4)	94.7(10)
F(6)-C(1)-F(4)	54.0(5)	F(5)-C(1)-F(4)	54.3(5)

TlAl(HFTB)₄? Is Tl⁺ eleven-coordinate, as implied in Table 2, or is it only ten-coordinate after discounting F19'', which is 3.471(10) Å from the Tl⁺ ion?

A particularly successful and straightforward approach for analyzing solid-state structures is the bond–valence method [69–71]. The valence of an atom (1 for Li⁺ or Tl⁺) is assumed to be

Table 10 (continued)

F(1)-C(1)-F(4)	69.1(6)	O(1)-C(1)-F(2)	90.7(8)
C(3)-C(1)-F(2)	142.6(12)	C(4)-C(1)-F(2)	91.2(9)
C(2)-C(1)-F(2)	31.0(8)	F(6)-C(1)-F(2)	174.7(8)
F(5)-C(1)-F(2)	122.1(7)	F(1)-C(1)-F(2)	52.5(5)
F(4)-C(1)-F(2)	121.6(7)	O(1)-C(1)-F(3)	137.4(10)
C(3)-C(1)-F(3)	94.2(10)	C(4)-C(1)-F(3)	91.3(10)
C(2)-C(1)-F(3)	30.3(7)	F(6)-C(1)-F(3)	122.4(7)
F(5)-C(1)-F(3)	68.9(5)	F(1)-C(1)-F(3)	52.4(5)
F(4)-C(1)-F(3)	91.7(6)	F(2)-C(1)-F(3)	53.2(5)
O(1)-C(1)-Tl	42.1(6)	C(3)-C(1)-Tl	81.5(9)
C(4)-C(1)-Tl	155.8(10)	C(2)-C(1)-Tl	87.4(8)
F(6)-C(1)-Tl	86.8(5)	F(5)-C(1)-Tl	107.8(5)
F(1)-C(1)-Tl	58.2(4)	F(4)-C(1)-Tl	53.7(4)
F(2)-C(1)-Tl	92.2(5)	F(3)-C(1)-Tl	109.8(5)
F(1)-C(2)-F(3)	106.2(15)	F(1)-C(2)-F(2)	105.5(14)
F(3)-C(2)-F(2)	108.5(14)	F(1)-C(2)-C(1)	111.2(14)
F(3)-C(2)-C(1)	113.2(14)	F(2)-C(2)-C(1)	111.8(15)
F(1)-C(2)-O(1)	90.8(10)	F(3)-C(2)-O(1)	147.0(13)
F(2)-C(2)-O(1)	93.2(10)	C(1)-C(2)-O(1)	33.9(7)
F(6)-C(3)-F(4)	106.5(14)	F(6)-C(3)-F(5)	104.1(14)
F(4)-C(3)-F(5)	106.9(13)	F(6)-C(3)-C(1)	111.2(14)
F(4)-C(3)-C(1)	114.5(14)	F(5)-C(3)-C(1)	113.0(14)
F(6)-C(3)-O(1)	93.8(10)	F(4)-C(3)-O(1)	93.2(10)
F(5)-C(3)-O(1)	147.6(12)	C(1)-C(3)-O(1)	34.7(7)
F(6)-C(3)-Tl	102.3(10)	F(4)-C(3)-Tl	45.5(7)
F(5)-C(3)-Tl	146.8(12)	C(1)-C(3)-Tl	75.0(8)
O(1)-C(3)-Tl	47.9(4)	C(1)-C(4)-O(1)	31.0(7)
O(2)-C(5)-C(8)	114.7(13)	O(2)-C(5)-C(7)	108.3(12)
C(8)-C(5)-C(7)	110.3(14)	O(2)-C(5)-C(6)	106.3(13)
C(8)-C(5)-C(6)	108.6(13)	C(7)-C(5)-C(6)	108.4(13)
O(2)-C(5)-F(11)	91.1(9)	C(8)-C(5)-F(11)	93.7(10)
C(7)-C(5)-F(11)	33.3(8)	C(6)-C(5)-F(11)	141.6(11)
O(2)-C(5)-F(8)	90.5(9)	C(8)-C(5)-F(8)	91.3(9)
C(7)-C(5)-F(8)	140.5(12)	C(6)-C(5)-F(8)	32.2(7)
F(11)-C(5)-F(8)	173.5(8)	O(2)-C(5)-F(10)	89.6(9)
C(8)-C(5)-F(10)	141.0(12)	C(7)-C(5)-F(10)	30.6(8)
C(6)-C(5)-F(10)	91.6(10)	F(11)-C(5)-F(10)	53.8(5)
F(8)-C(5)-F(10)	119.9(8)	O(2)-C(5)-F(12)	138.3(10)
C(8)-C(5)-F(12)	92.0(10)	C(7)-C(5)-F(12)	30.0(7)
C(6)-C(5)-F(12)	93.4(9)	F(11)-C(5)-F(12)	53.9(5)
F(8)-C(5)-F(12)	121.8(7)	F(10)-C(5)-F(12)	52.7(5)
O(2)-C(5)-F(9)	136.4(11)	C(8)-C(5)-F(9)	91.4(10)
C(7)-C(5)-F(9)	92.7(10)	C(6)-C(5)-F(9)	30.1(6)
F(11)-C(5)-F(9)	122.9(7)	F(8)-C(5)-F(9)	52.8(5)
F(10)-C(5)-F(9)	90.3(6)	F(12)-C(5)-F(9)	69.0(5)
O(2)-C(5)-F(7)	87.7(9)	C(8)-C(5)-F(7)	138.6(11)
C(7)-C(5)-F(7)	93.1(10)	C(6)-C(5)-F(7)	30.0(7)
F(11)-C(5)-F(7)	121.6(7)	F(8)-C(5)-F(7)	52.3(5)
F(10)-C(5)-F(7)	67.8(6)	F(12)-C(5)-F(7)	92.5(6)
F(9)-C(5)-F(7)	52.5(5)	O(2)-C(5)-Tl	40.8(7)
C(8)-C(5)-Tl	155.4(10)	C(7)-C(5)-Tl	86.0(9)
C(6)-C(5)-Tl	82.0(9)	F(11)-C(5)-Tl	90.5(5)
F(8)-C(5)-Tl	86.7(6)	F(10)-C(5)-Tl	57.5(4)
F(12)-C(5)-Tl	109.9(6)	F(9)-C(5)-Tl	106.6(6)
F(7)-C(5)-Tl	54.3(4)	F(9)-C(6)-F(7)	108.6(13)
F(9)-C(6)-F(8)	107.0(13)	F(7)-C(6)-F(8)	105.2(12)
F(9)-C(6)-C(5)	112.9(13)	F(7)-C(6)-C(5)	113.6(13)
F(8)-C(6)-C(5)	109.0(13)	F(9)-C(6)-O(2)	147.2(12)

distributed between the bonds it forms. Therefore, the individual bond valences, s , add up to the total valence of an atom or ion. By examin-

ing thousands of crystal structures, Brown and Shannon found that the following two-parameter empirical relationship could be used to cal-

Table 10 (continued)

F(7)-C(6)-O(2)	91.5(9)	F(8)-C(6)-O(2)	91.7(9)
C(5)-C(6)-O(2)	34.3(7)	F(9)-C(6)-T1	146.3(11)
F(7)-C(6)-T1	45.0(6)	F(8)-C(6)-T1	101.2(8)
C(5)-C(6)-T1	73.4(8)	O(2)-C(6)-T1	46.5(4)
F(12)-C(7)-F(10)	106.9(14)	F(12)-C(7)-F(11)	107.1(14)
F(10)-C(7)-F(11)	106.0(14)	F(12)-C(7)-C(5)	114.4(14)
F(10)-C(7)-C(5)	113.4(14)	F(11)-C(7)-C(5)	108.5(14)
F(12)-C(7)-O(2)	148.4(13)	F(10)-C(7)-O(2)	92.0(10)
F(11)-C(7)-O(2)	90.9(9)	C(5)-C(7)-O(2)	34.0(7)
C(5)-C(8)-O(2)	31.2(7)	O(3)-C(9)-C(10)	109.4(13)
O(3)-C(9)-C(12)	111.5(12)	C(10)-C(9)-C(12)	109.4(14)
O(3)-C(9)-C(11)	106.9(13)	C(10)-C(9)-C(11)	109.9(13)
C(12)-C(9)-C(11)	109.7(13)	O(3)-C(9)-F(15)	91.8(9)
C(10)-C(9)-F(15)	32.4(8)	C(12)-C(9)-F(15)	92.6(10)
C(11)-C(9)-F(15)	142.2(11)	O(3)-C(9)-F(14)	91.5(9)
C(10)-C(9)-F(14)	31.1(8)	C(12)-C(9)-F(14)	140.5(12)
C(11)-C(9)-F(14)	92.4(10)	F(15)-C(9)-F(14)	53.7(6)
O(3)-C(9)-F(17)	89.2(9)	C(10)-C(9)-F(17)	94.5(11)
C(12)-C(9)-F(17)	139.6(11)	C(11)-C(9)-F(17)	30.0(8)
F(15)-C(9)-F(17)	122.2(8)	F(14)-C(9)-F(17)	68.5(6)
O(3)-C(9)-F(18)	94.6(9)	C(10)-C(9)-F(18)	140.5(11)
C(12)-C(9)-F(18)	89.0(10)	C(11)-C(9)-F(18)	31.1(8)
F(15)-C(9)-F(18)	172.4(8)	F(14)-C(9)-F(18)	121.8(8)
F(17)-C(9)-F(18)	53.9(6)	O(3)-C(9)-F(16)	139.3(11)
C(10)-C(9)-F(16)	90.3(10)	C(12)-C(9)-F(16)	93.5(10)
C(11)-C(9)-F(16)	32.6(8)	F(15)-C(9)-F(16)	119.6(7)
F(14)-C(9)-F(16)	88.0(7)	F(17)-C(9)-F(16)	53.1(5)
F(18)-C(9)-F(16)	52.8(5)	O(3)-C(9)-F(13)	139.1(11)
C(10)-C(9)-F(13)	29.7(8)	C(12)-C(9)-F(13)	91.4(10)
C(11)-C(9)-F(13)	95.6(10)	F(15)-C(9)-F(13)	52.4(5)
F(14)-C(9)-F(13)	53.1(5)	F(17)-C(9)-F(13)	94.6(7)
F(18)-C(9)-F(13)	120.2(7)	F(16)-C(9)-F(13)	67.5(6)
F(14)-C(10)-F(13)	107.3(15)	F(14)-C(10)-F(15)	106.2(16)
F(13)-C(10)-F(15)	103.8(15)	F(14)-C(10)-C(9)	112.4(16)
F(13)-C(10)-C(9)	116.1(15)	F(15)-C(10)-C(9)	110.3(14)
F(14)-C(10)-O(3)	93.0(11)	F(13)-C(10)-O(3)	149.1(14)
F(15)-C(10)-O(3)	92.1(11)	C(9)-C(10)-O(3)	33.0(7)
F(17)-C(11)-F(18)	111.4(18)	F(17)-C(11)-F(16)	106.6(14)
F(18)-C(11)-F(16)	104.2(14)	F(17)-C(11)-C(9)	112.9(15)
F(18)-C(11)-C(9)	111.3(14)	F(16)-C(11)-C(9)	110.0(15)
F(17)-C(11)-O(3)	92.2(10)	F(18)-C(11)-O(3)	97.2(10)
F(16)-C(11)-O(3)	143.5(14)	C(9)-C(11)-O(3)	33.7(7)
C(9)-C(12)-O(3)	31.7(7)	O(4)-C(13)-C(15)	107.6(13)
O(4)-C(13)-C(16)	113.5(13)	C(15)-C(13)-C(16)	109.8(14)
O(4)-C(13)-C(14)	106.6(12)	C(15)-C(13)-C(14)	109.6(14)
C(16)-C(13)-C(14)	109.6(14)	O(4)-C(13)-F(21)	90.5(9)
C(15)-C(13)-F(21)	142.4(12)	C(16)-C(13)-F(21)	91.4(10)
C(14)-C(13)-F(21)	32.8(8)	O(4)-C(13)-F(22)	94.0(9)
C(15)-C(13)-F(22)	32.2(8)	C(16)-C(13)-F(22)	90.1(11)
C(14)-C(13)-F(22)	141.7(12)	F(21)-C(13)-F(22)	174.2(8)
O(4)-C(13)-F(20)	138.1(10)	C(15)-C(13)-F(20)	94.2(11)
C(16)-C(13)-F(20)	90.8(11)	C(14)-C(13)-F(20)	31.5(8)
F(21)-C(13)-F(20)	53.6(5)	F(22)-C(13)-F(20)	120.8(7)
O(4)-C(13)-F(19)	89.6(8)	C(15)-C(13)-F(19)	90.7(10)
C(16)-C(13)-F(19)	141.1(12)	C(14)-C(13)-F(19)	31.6(8)
F(21)-C(13)-F(19)	55.9(5)	F(22)-C(13)-F(19)	120.4(7)
F(20)-C(13)-F(19)	54.0(5)	O(4)-C(13)-F(23)	139.1(11)
C(15)-C(13)-F(23)	31.8(8)	C(16)-C(13)-F(23)	93.6(10)

culate s values, for a particular atom, that when added gave a sum that was within 0.05 valence units of the atom's valence [69]:

$$s = (r/r_0)^{-N} \quad \sum s = \text{atom's valence} \pm 0.05$$

The variable r is the experimentally determined interatomic distance for a particular bond (e.g., Li–O1, Li–O2, Li–F1, etc.). Self-consistent sets of parameters r_0 and N for many types of bonds have been determined [69]. For the four

Table 10 (continued)

C(14)-C(13)-F(23)	91.1(10)	F(21)-C(13)-F(23)	120.1(8)
F(22)-C(13)-F(23)	54.2(5)	F(20)-C(13)-F(23)	66.7(6)
F(19)-C(13)-F(23)	87.1(6)	O(4)-C(13)-F(24)	88.0(8)
C(15)-C(13)-F(24)	31.1(8)	C(16)-C(13)-F(24)	140.9(12)
C(14)-C(13)-F(24)	93.4(11)	F(21)-C(13)-F(24)	122.0(7)
F(22)-C(13)-F(24)	54.7(5)	F(20)-C(13)-F(24)	93.8(7)
F(19)-C(13)-F(24)	66.1(5)	F(23)-C(13)-F(24)	53.7(5)
F(20)-C(14)-F(21)	104.8(15)	F(20)-C(14)-F(19)	107.0(14)
F(21)-C(14)-F(19)	110.7(14)	F(20)-C(14)-C(13)	112.2(14)
F(21)-C(14)-C(13)	109.5(14)	F(19)-C(14)-C(13)	112.3(15)
F(20)-C(14)-O(4)	147.3(12)	F(21)-C(14)-O(4)	91.8(10)
F(19)-C(14)-O(4)	92.5(10)	C(13)-C(14)-O(4)	35.1(7)
F(24)-C(15)-F(22)	107.3(15)	F(24)-C(15)-F(23)	105.0(14)
F(22)-C(15)-F(23)	105.3(14)	F(24)-C(15)-C(13)	113.9(14)
F(22)-C(15)-C(13)	111.9(14)	F(23)-C(15)-C(13)	112.9(15)
F(24)-C(15)-O(4)	91.2(10)	F(22)-C(15)-O(4)	96.3(10)
F(23)-C(15)-O(4)	147.4(14)	C(13)-C(15)-O(4)	34.9(7)
C(13)-C(16)-O(4)	32.1(7)	C(2)-F(1)-F(2)	37.4(9)
C(2)-F(1)-F(3)	36.9(9)	F(2)-F(1)-F(3)	61.2(5)
C(2)-F(1)-C(1)	37.6(9)	F(2)-F(1)-C(1)	64.1(5)
F(3)-F(1)-C(1)	64.5(5)	C(2)-F(1)-F(4)	87.4(10)
F(2)-F(1)-F(4)	119.6(5)	F(3)-F(1)-F(4)	90.3(5)
C(1)-F(1)-F(4)	55.5(4)	C(2)-F(1)-O(1)	60.2(9)
F(2)-F(1)-O(1)	68.8(5)	F(3)-F(1)-O(1)	93.4(4)
C(1)-F(1)-O(1)	30.5(4)	F(4)-F(1)-O(1)	60.7(4)
C(2)-F(1)-Tl	115.9(10)	F(2)-F(1)-Tl	114.1(5)
F(3)-F(1)-Tl	144.1(5)	C(1)-F(1)-Tl	81.3(4)
F(4)-F(1)-Tl	59.9(3)	O(1)-F(1)-Tl	55.8(3)
C(2)-F(1)-Tl#3	90.5(10)	F(2)-F(1)-Tl#3	53.1(4)
F(3)-F(1)-Tl#3	105.3(5)	C(1)-F(1)-Tl#3	108.8(5)
F(4)-F(1)-Tl#3	150.6(4)	O(1)-F(1)-Tl#3	93.1(4)
Tl-F(1)-Tl#3	95.3(3)	C(2)-F(2)-F(1)	37.1(9)
C(2)-F(2)-F(3)	35.6(8)	F(1)-F(2)-F(3)	59.5(5)
C(2)-F(2)-C(1)	37.2(9)	F(1)-F(2)-C(1)	63.4(5)
F(3)-F(2)-C(1)	63.7(5)	C(2)-F(2)-O(1)	58.3(9)
F(1)-F(2)-O(1)	66.2(4)	F(3)-F(2)-O(1)	91.2(5)
C(1)-F(2)-O(1)	29.9(4)	C(2)-F(2)-Tl#3	133.8(10)
F(1)-F(2)-Tl#3	96.7(5)	F(3)-F(2)-Tl#3	137.2(5)
C(1)-F(2)-Tl#3	140.6(5)	O(1)-F(2)-Tl#3	112.2(4)
C(2)-F(3)-F(1)	36.9(9)	C(2)-F(3)-F(2)	35.9(9)
F(1)-F(3)-F(2)	59.3(5)	C(2)-F(3)-C(1)	36.5(9)
F(1)-F(3)-C(1)	63.1(5)	F(2)-F(3)-C(1)	63.1(5)
C(2)-F(3)-F(5)	87.0(10)	F(1)-F(3)-F(5)	90.9(5)
F(2)-F(3)-F(5)	118.2(5)	C(1)-F(3)-F(5)	55.1(4)
C(3)-F(4)-F(6)	36.6(8)	C(3)-F(4)-F(5)	36.9(8)
F(6)-F(4)-F(5)	59.0(5)	C(3)-F(4)-C(1)	34.7(8)
F(6)-F(4)-C(1)	61.7(5)	F(5)-F(4)-C(1)	62.8(5)
C(3)-F(4)-F(1)	84.9(9)	F(6)-F(4)-F(1)	117.1(5)
F(5)-F(4)-F(1)	89.9(5)	C(1)-F(4)-F(1)	55.4(5)
C(3)-F(4)-O(1)	57.6(8)	F(6)-F(4)-O(1)	67.2(4)
F(5)-F(4)-O(1)	91.6(4)	C(1)-F(4)-O(1)	30.3(4)
F(1)-F(4)-O(1)	60.2(4)	C(3)-F(4)-F(11)#1	151.8(11)
F(6)-F(4)-F(11)#1	171.4(6)	F(5)-F(4)-F(11)#1	126.1(6)
C(1)-F(4)-F(11)#1	126.1(6)	F(1)-F(4)-F(11)#1	70.9(4)
O(1)-F(4)-F(11)#1	117.4(4)	C(3)-F(4)-Tl	115.5(9)
F(6)-F(4)-Tl	110.9(5)	F(5)-F(4)-Tl	147.9(5)
C(1)-F(4)-Tl	85.3(4)	F(1)-F(4)-Tl	67.0(3)
O(1)-F(4)-Tl	58.0(3)	F(11)#1-F(4)-Tl	68.7(3)

types of bonds to be discussed below, these parameters are: Li–O, $r_0 = 1.378$, $N = 4.065$; Li–F, $r_0 = 1.288$, $N = 3.9$; Tl–O, $r_0 = 2.100$,

$N = 6$; Tl–F, $r_0 = 1.993$, $N = 6$. The parameter r_0 can be thought of as the length of a bond of unit valence, although the relationship $s =$

Table 10 (continued)

C(3)-F(5)-F(6)	37.4(9)	C(3)-F(5)-F(4)	36.2(8)
F(6)-F(5)-F(4)	59.7(5)	C(3)-F(5)-C(1)	35.2(8)
F(6)-F(5)-C(1)	62.0(5)	F(4)-F(5)-C(1)	62.9(5)
C(3)-F(5)-F(3)	85.1(9)	F(6)-F(5)-F(3)	118.0(5)
F(4)-F(5)-F(3)	88.9(5)	C(1)-F(5)-F(3)	56.1(5)
C(3)-F(5)-F(5)#4	92.0(9)	F(6)-F(5)-F(5)#4	74.7(5)
F(4)-F(5)-F(5)#4	70.1(5)	C(1)-F(5)-F(5)#4	127.2(7)
F(3)-F(5)-F(5)#4	146.2(7)	C(3)-F(6)-F(5)	38.5(8)
C(3)-F(6)-F(4)	36.9(9)	F(5)-F(6)-F(4)	61.3(5)
C(3)-F(6)-C(1)	36.6(8)	F(5)-F(6)-C(1)	64.5(5)
F(4)-F(6)-C(1)	64.3(5)	C(3)-F(6)-O(1)	57.4(8)
F(5)-F(6)-O(1)	92.6(5)	F(4)-F(6)-O(1)	67.0(4)
C(1)-F(6)-O(1)	30.2(4)	C(3)-F(6)-F(18)	132.3(10)
F(5)-F(6)-F(18)	132.0(6)	F(4)-F(6)-F(18)	151.0(5)
C(1)-F(6)-F(18)	96.4(5)	O(1)-F(6)-F(18)	85.4(4)
C(3)-F(6)-T1	59.7(8)	F(5)-F(6)-T1	96.3(4)
F(4)-F(6)-T1	40.7(3)	C(1)-F(6)-T1	59.5(4)
O(1)-F(6)-T1	40.4(2)	F(18)-F(6)-T1	111.5(3)
C(6)-F(7)-F(8)	37.5(8)	C(6)-F(7)-F(9)	35.4(7)
F(8)-F(7)-F(9)	59.9(5)	C(6)-F(7)-C(5)	36.4(8)
F(8)-F(7)-C(5)	62.4(5)	F(9)-F(7)-C(5)	63.2(5)
C(6)-F(7)-F(10)	85.2(9)	F(8)-F(7)-F(10)	117.7(5)
F(9)-F(7)-F(10)	88.8(5)	C(5)-F(7)-F(10)	55.4(4)
C(6)-F(7)-O(2)	59.8(7)	F(8)-F(7)-O(2)	67.7(4)
F(9)-F(7)-O(2)	92.2(5)	C(5)-F(7)-O(2)	30.5(4)
F(10)-F(7)-O(2)	60.9(4)	C(6)-F(7)-T1	116.6(8)
F(8)-F(7)-T1	111.2(5)	F(9)-F(7)-T1	146.5(5)
C(5)-F(7)-T1	83.9(5)	F(10)-F(7)-T1	66.2(3)
O(2)-F(7)-T1	56.8(3)	C(6)-F(8)-F(7)	37.2(8)
C(6)-F(8)-F(9)	36.1(7)	F(7)-F(8)-F(9)	60.6(5)
C(6)-F(8)-C(5)	38.8(8)	F(7)-F(8)-C(5)	65.3(5)
F(9)-F(8)-C(5)	64.4(5)	C(6)-F(8)-O(2)	59.4(7)
F(7)-F(8)-O(2)	67.2(4)	F(9)-F(8)-O(2)	92.3(4)
C(5)-F(8)-O(2)	30.4(4)	C(6)-F(9)-F(8)	36.9(8)
C(6)-F(9)-F(7)	36.0(8)	F(8)-F(9)-F(7)	59.5(5)
C(6)-F(9)-C(5)	37.0(9)	F(8)-F(9)-C(5)	62.8(5)
F(7)-F(9)-C(5)	64.3(5)	C(6)-F(9)-F(12)	86.3(9)
F(8)-F(9)-F(12)	118.0(5)	F(7)-F(9)-F(12)	90.8(5)
C(5)-F(9)-F(12)	55.2(4)	C(7)-F(10)-F(12)	36.4(8)
C(7)-F(10)-F(11)	37.5(8)	F(12)-F(10)-F(11)	60.5(5)
C(7)-F(10)-C(5)	36.0(9)	F(12)-F(10)-C(5)	63.8(5)
F(11)-F(10)-C(5)	62.0(5)	C(7)-F(10)-F(7)	87.3(9)
F(12)-F(10)-F(7)	92.1(5)	F(11)-F(10)-F(7)	118.9(5)
C(5)-F(10)-F(7)	56.9(5)	C(7)-F(10)-O(2)	59.3(8)
F(12)-F(10)-O(2)	92.7(5)	F(11)-F(10)-O(2)	66.9(4)
C(5)-F(10)-O(2)	30.5(4)	F(7)-F(10)-O(2)	60.8(3)
C(7)-F(10)-T1	114.4(9)	F(12)-F(10)-T1	144.8(5)
F(11)-F(10)-T1	110.5(5)	C(5)-F(10)-T1	81.8(5)
F(7)-F(10)-T1	61.2(3)	O(2)-F(10)-T1	55.2(3)
C(7)-F(11)-F(10)	36.6(9)	C(7)-F(11)-F(12)	35.8(8)
F(10)-F(11)-F(12)	59.3(5)	C(7)-F(11)-C(5)	38.2(9)
F(10)-F(11)-C(5)	64.2(6)	F(12)-F(11)-C(5)	64.3(5)
C(7)-F(11)-O(2)	59.6(8)	F(10)-F(11)-O(2)	67.3(4)
F(12)-F(11)-O(2)	92.4(5)	C(5)-F(11)-O(2)	30.6(4)
C(7)-F(11)-F(4)#3	105.8(10)	F(10)-F(11)-F(4)#3	85.5(5)
F(12)-F(11)-F(4)#3	84.2(4)	C(5)-F(11)-F(4)#3	144.0(6)
O(2)-F(11)-F(4)#3	149.8(6)	C(7)-F(11)-T1#3	137.6(10)
F(10)-F(11)-T1#3	101.1(5)	F(12)-F(11)-T1#3	138.6(5)

$(r/r_0)^{-N}$ may only be valid over the central part of the range of r values for a given bond type. For example, note that the experimental

Li–F distance in gaseous, diatomic LiF is 1.5639 Å [72], but $r_0(\text{Li–F})$ is 1.288 Å [69]. However, the sum of bond valences for crystalline LiF,

Table 10 (continued)

C(5)-F(11)-T1#3	144.1(6)	O(2)-F(11)-T1#3	114.3(4)
F(4)#3-F(11)-T1#3	56.6(3)	C(7)-F(12)-F(10)	36.7(9)
C(7)-F(12)-F(11)	37.1(9)	F(10)-F(12)-F(11)	60.2(5)
C(7)-F(12)-C(5)	35.5(9)	F(10)-F(12)-C(5)	63.5(5)
F(11)-F(12)-C(5)	61.8(5)	C(7)-F(12)-F(9)	84.8(9)
F(10)-F(12)-F(9)	88.3(5)	F(11)-F(12)-F(9)	117.4(5)
C(5)-F(12)-F(9)	55.7(5)	C(10)-F(13)-F(15)	38.2(9)
C(10)-F(13)-F(14)	36.1(9)	F(15)-F(13)-F(14)	60.1(6)
C(10)-F(13)-C(9)	34.2(9)	F(15)-F(13)-C(9)	61.9(5)
F(14)-F(13)-C(9)	61.9(5)	C(10)-F(13)-F(16)	83.2(10)
F(15)-F(13)-F(16)	117.6(6)	F(14)-F(13)-F(16)	86.0(6)
C(9)-F(13)-F(16)	55.9(5)	C(10)-F(14)-F(15)	37.3(10)
C(10)-F(14)-F(13)	36.7(9)	F(15)-F(14)-F(13)	59.2(6)
C(10)-F(14)-C(9)	36.5(10)	F(15)-F(14)-C(9)	62.9(6)
F(13)-F(14)-C(9)	65.0(6)	C(10)-F(14)-F(17)	87.3(11)
F(15)-F(14)-F(17)	118.9(6)	F(13)-F(14)-F(17)	93.9(6)
C(9)-F(14)-F(17)	56.0(5)	C(10)-F(14)-O(3)	58.5(10)
F(15)-F(14)-O(3)	67.1(5)	F(13)-F(14)-O(3)	92.7(5)
C(9)-F(14)-O(3)	29.6(4)	F(17)-F(14)-O(3)	60.2(4)
C(10)-F(15)-F(13)	38.0(9)	C(10)-F(15)-F(14)	36.5(10)
F(13)-F(15)-F(14)	60.7(6)	C(10)-F(15)-C(9)	37.4(9)
F(13)-F(15)-C(9)	65.7(6)	F(14)-F(15)-C(9)	63.4(6)
C(10)-F(15)-O(3)	58.8(9)	F(13)-F(15)-O(3)	93.6(5)
F(14)-F(15)-O(3)	67.4(5)	C(9)-F(15)-O(3)	29.6(4)
C(11)-F(16)-F(18)	36.9(9)	C(11)-F(16)-F(17)	35.3(8)
F(18)-F(16)-F(17)	60.6(6)	C(11)-F(16)-C(9)	37.4(9)
F(18)-F(16)-C(9)	62.9(5)	F(17)-F(16)-C(9)	62.7(5)
C(11)-F(16)-F(13)	89.6(10)	F(18)-F(16)-F(13)	119.4(6)
F(17)-F(16)-F(13)	93.4(6)	C(9)-F(16)-F(13)	56.6(5)
C(11)-F(17)-F(16)	38.2(9)	C(11)-F(17)-F(18)	34.7(10)
F(16)-F(17)-F(18)	59.5(6)	C(11)-F(17)-C(9)	37.1(9)
F(16)-F(17)-C(9)	64.2(5)	F(18)-F(17)-C(9)	63.1(5)
C(11)-F(17)-F(14)	86.2(11)	F(16)-F(17)-F(14)	86.5(6)
F(18)-F(17)-F(14)	118.1(6)	C(9)-F(17)-F(14)	55.5(5)
C(11)-F(17)-O(3)	59.6(9)	F(16)-F(17)-O(3)	93.2(5)
F(18)-F(17)-O(3)	70.0(5)	C(9)-F(17)-O(3)	30.0(4)
F(14)-F(17)-O(3)	61.6(4)	C(11)-F(17)-F(17)#5	164.2(15)
F(16)-F(17)-F(17)#5	140.8(9)	F(18)-F(17)-F(17)#5	157.8(10)
C(9)-F(17)-F(17)#5	128.1(8)	F(14)-F(17)-F(17)#5	78.1(7)
O(3)-F(17)-F(17)#5	110.1(6)	C(11)-F(18)-F(16)	38.9(9)
C(11)-F(18)-F(17)	33.9(10)	F(16)-F(18)-F(17)	59.9(6)
C(11)-F(18)-C(9)	37.6(9)	F(16)-F(18)-C(9)	64.3(6)
F(17)-F(18)-C(9)	63.0(6)	C(11)-F(18)-O(3)	55.3(8)
F(16)-F(18)-O(3)	90.3(5)	F(17)-F(18)-O(3)	64.5(5)
C(9)-F(18)-O(3)	28.6(4)	C(11)-F(18)-F(6)	144.7(10)
F(16)-F(18)-F(6)	142.9(7)	F(17)-F(18)-F(6)	151.7(7)
C(9)-F(18)-F(6)	107.1(5)	O(3)-F(18)-F(6)	94.0(4)
C(14)-F(19)-F(20)	36.4(8)	C(14)-F(19)-F(21)	34.6(8)
F(20)-F(19)-F(21)	58.1(5)	C(14)-F(19)-C(13)	36.1(9)
F(20)-F(19)-C(13)	62.8(5)	F(21)-F(19)-C(13)	61.1(5)
C(14)-F(19)-F(24)	89.0(9)	F(20)-F(19)-F(24)	93.4(5)
F(21)-F(19)-F(24)	118.2(5)	C(13)-F(19)-F(24)	57.2(5)
C(14)-F(19)-O(4)	58.3(8)	F(20)-F(19)-O(4)	91.6(5)
F(21)-F(19)-O(4)	65.9(4)	C(13)-F(19)-O(4)	30.7(4)
F(24)-F(19)-O(4)	61.3(4)	C(14)-F(19)-T1#3	135.3(10)
F(20)-F(19)-T1#3	157.8(6)	F(21)-F(19)-T1#3	104.8(5)
C(13)-F(19)-T1#3	124.2(5)	F(24)-F(19)-T1#3	107.9(4)
O(4)-F(19)-T1#3	93.5(4)	C(14)-F(19)-T1#6	103.9(9)

with six Li–F distances of 2.009 Å, is 1.06. Note also that the calculated (3-21G) Li–F distance in $[\text{H}_3\text{CF-Li}]^+$ is 1.658 Å [54].

One of the virtues of the bond–valence method is that the bond–valence distribution in a compound can be determined from its crystal

Table 10 (continued)

F(20)-F(19)-Tl#6	68.3(4)	F(21)-F(19)-Tl#6	108.1(4)
C(13)-F(19)-Tl#6	127.0(5)	F(24)-F(19)-Tl#6	108.7(4)
O(4)-F(19)-Tl#6	157.7(4)	Tl#3-F(19)-Tl#6	108.8(2)
C(14)-F(20)-F(21)	37.7(9)	C(14)-F(20)-F(19)	36.6(9)
F(21)-F(20)-F(19)	62.2(5)	C(14)-F(20)-C(13)	36.3(9)
F(21)-F(20)-C(13)	62.4(5)	F(19)-F(20)-C(13)	63.2(5)
C(14)-F(20)-F(23)	85.9(10)	F(21)-F(20)-F(23)	119.2(6)
F(19)-F(20)-F(23)	86.4(6)	C(13)-F(20)-F(23)	57.0(5)
C(14)-F(20)-Tl#6	110.7(10)	F(21)-F(20)-Tl#6	115.2(5)
F(19)-F(20)-Tl#6	74.9(4)	C(13)-F(20)-Tl#6	133.3(6)
F(23)-F(20)-Tl#6	102.8(5)	C(14)-F(21)-F(20)	37.5(9)
C(14)-F(21)-F(19)	34.7(8)	F(20)-F(21)-F(19)	59.6(5)
C(14)-F(21)-C(13)	37.7(9)	F(20)-F(21)-C(13)	64.0(5)
F(19)-F(21)-C(13)	63.0(5)	C(14)-F(21)-O(4)	58.9(8)
F(20)-F(21)-O(4)	92.8(5)	F(19)-F(21)-O(4)	66.7(4)
C(13)-F(21)-O(4)	30.9(4)	C(15)-F(22)-F(23)	37.5(8)
C(15)-F(22)-F(24)	36.2(9)	F(23)-F(22)-F(24)	59.4(5)
C(15)-F(22)-C(13)	35.9(8)	F(23)-F(22)-C(13)	63.3(6)
F(24)-F(22)-C(13)	63.1(5)	C(15)-F(22)-O(4)	55.2(8)
F(23)-F(22)-O(4)	90.0(5)	F(24)-F(22)-O(4)	64.3(4)
C(13)-F(22)-O(4)	29.6(4)	C(15)-F(23)-F(24)	37.3(9)
C(15)-F(23)-F(22)	37.3(9)	F(24)-F(23)-F(22)	60.7(5)
C(15)-F(23)-C(13)	35.3(9)	F(24)-F(23)-C(13)	63.2(5)
F(22)-F(23)-C(13)	62.5(6)	C(15)-F(23)-F(20)	87.4(10)
F(24)-F(23)-F(20)	93.0(5)	F(22)-F(23)-F(20)	118.7(6)
C(13)-F(23)-F(20)	56.3(5)	C(15)-F(24)-F(23)	37.8(8)
C(15)-F(24)-F(22)	36.5(9)	F(23)-F(24)-F(22)	59.9(5)
C(15)-F(24)-C(13)	35.0(8)	F(23)-F(24)-C(13)	63.1(5)
F(22)-F(24)-C(13)	62.2(5)	C(15)-F(24)-F(19)	85.2(9)
F(23)-F(24)-F(19)	86.8(5)	F(22)-F(24)-F(19)	118.7(5)
C(13)-F(24)-F(19)	56.8(5)	C(15)-F(24)-O(4)	59.2(8)
F(23)-F(24)-O(4)	93.2(5)	F(22)-F(24)-O(4)	69.5(4)
C(13)-F(24)-O(4)	31.0(4)	F(19)-F(24)-O(4)	62.2(4)

Symmetry transformations used to generate equivalent atoms: #1 $-x+2, y-1/2, -z+1/2$; #2 $x, y-1, z$; #3 $-x+2, y+1/2, -z+1/2$; #4 $-x+2, -y, -z$; #5 $-x+1, -y+1, -z$; #6 $x, y+1, z$.

structure. The method is particularly useful for analyzing structures with many long, weak bonds. In an important study, Caulton and co-workers found that the sum of bond valences for the symmetry-related, twelve-coordinate Tl^+ ions in $Tl_2Zr(HFIP)_6$ was 1.05, only 5% higher than the expected valence of 1 [34]. The three $Tl-O$ bond valences of 0.203, 0.173, and 0.167, comprised only 52% of the total valence of Tl^+ . The network of relatively longer and weaker $Tl-F$ bonds, which ranged in distance from 3.13 to 3.44 Å and which ranged in bond valence from 0.066 to 0.038, provided the other 48% of the total valence.

Bond valences for the metal–oxygen and metal–fluorine bonds in $LiAl(HFPP)_4$, $TlAl(HFTB)_4$, and $TlAl(HFIP)_4$ are listed in Table 19. For all three compounds, the sum of bond valences is within 6% of 1.00. For all three compounds, the oxygen donors provide only about $45 \pm 3\%$ of the total bond valence. This is true even for $TlAl(HFIP)_4$, which has three $Tl-O$ bonds. Therefore, the $M-F(C)$ bonds provide more than half the stabilization of the cations in the three compounds. For $LiAl(HFPP)_4$, lengthening a $Li-F(C)$ bond by 19%, from 1.984 to 2.354 Å, results in a 50% decrease in bond valence, from 0.185 to 0.095.

If the Li^+ ion were in a symmetrical geometry with six bonds providing identical bond valences, each bond valence would be 0.167. Three of the four $\text{Li}-\text{F}(\text{C})$ bonds are at about this value, which indicates that they are quite nor-

mal metal–ligand bonds for six-coordinate Li^+ , not just weak, secondary interactions. For $\text{TlAl}(\text{HFTB})_4$, the greater number of $\text{Tl}-\text{F}(\text{C})$ bonds necessitates that each has a smaller bond valence. In fact, the largest $\text{Tl}-\text{F}(\text{C})$ bond va-

Table 11
Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{TlAl}(\text{OC}(\text{CH}_3)(\text{CF}_3)_2)_4$

	U11	U22	U33	U23	U13	U12
Tl	35(1)	29(1)	34(1)	6(1)	4(1)	6(1)
Al	20(2)	20(2)	19(2)	-1(2)	-2(2)	0(2)
O(1)	26(6)	21(6)	17(5)	-3(4)	5(4)	2(5)
O(2)	18(5)	30(6)	16(5)	0(4)	0(4)	0(5)
O(3)	15(5)	26(6)	32(6)	-13(5)	-2(4)	-1(5)
O(4)	27(6)	21(6)	29(6)	-5(5)	0(5)	3(5)
C(1)	30(9)	19(8)	20(8)	2(6)	3(7)	0(7)
C(2)	48(12)	43(11)	26(9)	10(9)	14(9)	1(10)
C(3)	39(11)	31(9)	47(11)	-8(8)	9(9)	7(9)
C(4)	53(11)	23(10)	33(9)	9(7)	9(8)	14(8)
C(5)	19(8)	38(10)	31(9)	2(8)	-12(7)	-16(8)
C(6)	38(10)	36(9)	16(8)	-5(7)	11(7)	-7(9)
C(7)	39(11)	35(10)	33(10)	1(8)	9(8)	-10(9)
C(8)	20(8)	39(10)	45(10)	2(9)	4(7)	5(8)
C(10)	48(12)	38(12)	48(12)	3(9)	-3(9)	3(10)
C(11)	39(11)	32(9)	32(9)	-10(7)	-16(8)	8(8)
C(12)	45(10)	16(8)	52(10)	-1(9)	-12(8)	-14(9)
C(13)	7(7)	27(8)	39(9)	12(7)	-1(7)	7(7)
C(14)	52(12)	26(10)	51(12)	0(9)	-15(10)	9(9)
C(15)	54(13)	22(9)	50(12)	20(9)	2(10)	2(9)
C(16)	39(11)	39(10)	55(12)	2(9)	-10(9)	1(9)
F(1)	41(6)	83(8)	47(6)	26(6)	-17(5)	-7(6)
F(2)	40(6)	51(7)	68(7)	-24(6)	7(6)	-14(5)
F(3)	22(5)	54(6)	60(7)	5(5)	11(5)	-5(5)
F(4)	72(8)	44(7)	32(5)	2(5)	0(5)	36(6)
F(5)	73(8)	41(6)	47(6)	-10(5)	32(6)	12(5)
F(6)	55(6)	26(5)	50(6)	-6(5)	-2(5)	0(6)
F(7)	49(7)	44(7)	59(7)	17(5)	13(5)	-1(5)
F(8)	56(6)	31(6)	54(6)	1(5)	-7(5)	-24(5)
F(9)	67(8)	56(7)	47(6)	3(5)	33(6)	-14(6)
F(10)	37(6)	74(8)	54(7)	1(6)	-24(5)	2(6)
F(11)	51(7)	63(7)	50(6)	-2(6)	-16(5)	-40(6)
F(12)	66(7)	91(9)	18(5)	-21(5)	-2(5)	-12(7)
F(13)	30(6)	66(8)	94(9)	-25(7)	-8(6)	-11(6)
F(14)	40(7)	55(8)	133(12)	-17(8)	-3(7)	15(6)
F(15)	38(6)	127(12)	59(8)	-24(8)	11(6)	-12(7)
F(16)	79(9)	60(8)	50(7)	-9(6)	-21(6)	-14(7)
F(17)	117(11)	38(7)	64(8)	13(6)	-37(8)	3(7)
F(18)	57(8)	100(10)	47(7)	-5(7)	-2(6)	15(8)
F(19)	19(5)	48(6)	62(6)	-16(5)	-8(4)	-14(5)
F(20)	86(9)	31(6)	89(9)	-7(6)	-35(7)	18(6)
F(21)	62(7)	47(6)	36(6)	-8(5)	-3(5)	-8(6)
F(22)	68(8)	52(7)	47(6)	6(5)	-9(6)	5(6)
F(23)	92(10)	48(7)	69(8)	10(6)	13(7)	21(7)
F(24)	43(6)	53(7)	49(6)	-1(5)	21(5)	-6(5)

The anisotropic displacement factor exponent takes the form: $-2\pi^2((ha^*)^2U_{11} + \dots + 2hka^*b^*U_{12})$.

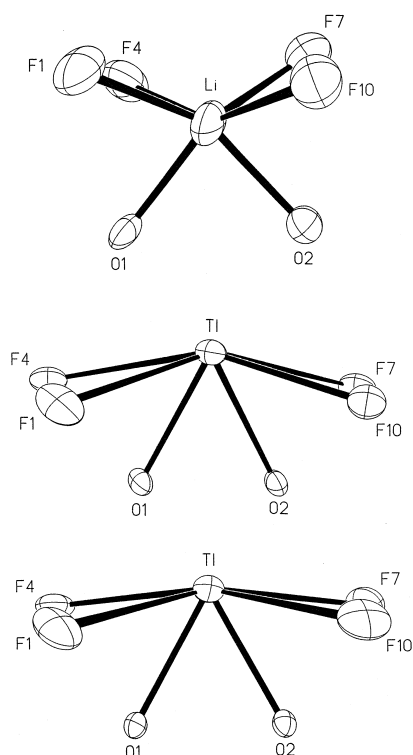


Fig. 3. Drawings of the MO_2F_4 coordination units formed by the hexadentate $\text{Al}(\text{OCR}(\text{CF}_3)_2)_4^-$ anions in the structures of $\text{LiAl}(\text{OC}(\text{Ph})(\text{CF}_3)_2)_4$ (top, $\text{R} = \text{Ph}$), $\text{TlAl}(\text{OC}(\text{CH}_3)(\text{CF}_3)_2)_4$ (middle, $\text{R} = \text{CH}_3$) and $\text{TlAl}(\text{OCH}(\text{CF}_3)_2)_4$ (bottom, $\text{R} = \text{H}$) (50% probability ellipsoids). The dihedral angles of the planes formed by the $\text{O}_1\text{—F}_1\text{—F}_4$ and $\text{O}_2\text{—F}_7\text{—F}_{10}$ triangles are 12° (top), 111° (middle) and 85° (bottom).

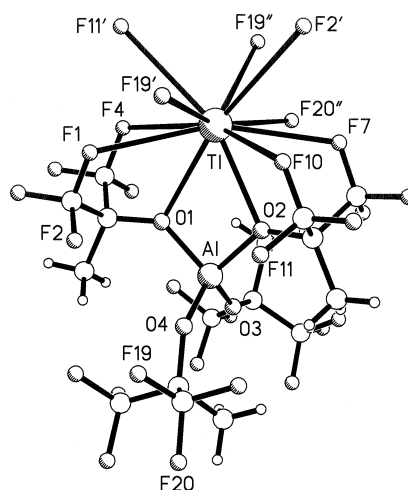


Fig. 4. Drawing of the structure of $\text{TlAl}(\text{OC}(\text{CH}_3)(\text{CF}_3)_2)_4$. The unlabeled shaded circles are fluorine atoms, while the unlabeled open circles are carbon atoms. Selected interatomic distances (\AA) and angles (deg): Tl—O_1 , 2.731(9); Tl—O_2 , 2.717(9); Tl—F_1 , 3.087(10); Tl—F_4 , 2.903(9); Tl—F_7 , 2.952(10); Tl—F_{10} , 3.081(11); other Tl—F , 3.154(10) to 3.471(10) \AA ; $\text{O}_1\text{—Tl—O}_2$, 57.9(3).

lence, 0.105 for Tl—F_4 , is only slightly larger than the smallest $\text{Li—F}(\text{C})$ bond valence in $\text{LiAl}(\text{HFPP})_4$. This is necessary because of the much larger size of Tl^+ than Li^+ . If a Tl^+ ion were substituted for the Li^+ ion in the structure of $\text{LiAl}(\text{HFPP})_4$, and the set of Tl—O and Tl—F

Table 12

Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{TlAl}(\text{OC}(\text{CH}_3)(\text{CF}_3)_2)_4$

	x	y	z	U(eq)
H(4A)	8140(14)	3396(15)	119(7)	80
H(4C)	8757(14)	4626(15)	422(7)	80
H(4B)	9303(14)	3691(15)	-52(7)	80
H(8A)	6585(11)	4771(17)	2769(8)	80
H(8B)	5785(11)	3596(17)	2616(8)	80
H(8C)	6077(11)	4010(17)	3319(8)	80
H(12A)	5985(13)	762(16)	1578(8)	80
H(12B)	5562(13)	266(16)	906(8)	80
H(12C)	6726(13)	797(16)	1016(8)	80
H(16A)	5896(13)	6173(18)	1876(9)	80
H(16B)	5883(13)	7365(18)	1395(9)	80
H(16C)	5885(13)	5882(18)	1151(9)	80

distances were kept the same as the set of Li–O and Li–F distances, the sum of Ti–O and Ti–F bond valences would be 5.82.

Plots of $s(\text{Li–F})$ vs. $r(\text{Li–F})$ and $s(\text{Ti–F})$ vs.

$r(\text{Ti–F})$ are shown in Fig. 7. Also included in each plot is a point for a bond valence of 1.00 at the r_0 value and points for bond valences of 0.03 and 0.01, which occur at 3.17 and 4.20 Å,

Table 13

Crystal data and structure refinement for $\text{TlAl}(\text{OC}(\text{H})(\text{CF}_3)_2)_4$

Identification code	shs67
Empirical formula	$\text{C}_{12}\text{H}_4\text{AlF}_{24}\text{O}_4\text{Tl}$
Formula weight	899.50
Temperature	143(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	$a = 14.2609(14)$ Å $\alpha = 90^\circ$ $b = 9.8024(9)$ Å $\beta = 93.467(8)^\circ$ $c = 16.911(2)$ Å $\gamma = 90^\circ$
Volume, Z	$2359.6(4)$ Å ³ , 4
Density (calculated)	2.532 Mg/m ³
Absorption coefficient	7.092 mm ⁻¹
F(000)	1672
Crystal size	0.28 x 0.28 x 0.48 mm
θ range for data collection	1.81 to 29.97°
Limiting indices	$-1 \leq h \leq 18$, $-1 \leq k \leq 13$, $-21 \leq l \leq 23$
Reflections collected	6768
Independent reflections	5439 ($R_{\text{int}} = 0.0709$)
Absorption correction	Semi-empirical from psi-scans
Max. and min. transmission	0.2311 and 0.1296
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5439 / 0 / 384
Goodness-of-fit on F^2	1.028
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0533$, $wR2 = 0.1031$
R indices (all data)	$R1 = 0.1118$, $wR2 = 0.1261$
Extinction coefficient	0.0
Largest diff. peak and hole	1.576 and -1.669 eÅ ⁻³

respectively, for Li–F and at 3.58 and 4.29 Å, respectively, for Ti–F. The compound LiAl(HFPP)₄ exhibits a rapid intramolecular rearrangement in solution: its ¹⁹F NMR spectrum

at 25°C exhibits 24 equivalent fluorine atoms coupled to lithium with an apparent $J(^7\text{Li}-^{19}\text{F})$ coupling constant of 14.4 Hz [13]. The upper plot in Fig. 7 indicates how dissociation of the

Table 14

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for TiAl(OC(H)(CF₃)₂)₄

	x	y	z	U(eq)
Ti1	7183(1)	8835(1)	2230(1)	29(1)
Al1	5445(2)	6217(3)	2692(1)	20(1)
O(1)	5747(5)	6970(6)	1808(3)	27(2)
O(2)	6197(5)	7202(6)	3304(3)	27(2)
O(3)	5764(4)	4485(6)	2726(3)	25(1)
O(4)	4283(4)	6199(7)	2867(4)	35(2)
C(1)	5342(7)	6893(9)	1038(5)	27(2)
C(2)	5016(9)	8293(10)	797(6)	40(3)
C(3)	6044(7)	6278(12)	506(6)	39(2)
C(4)	6298(7)	7385(9)	4122(5)	22(2)
C(5)	7236(8)	6847(10)	4435(5)	31(2)
C(6)	6184(7)	8913(11)	4282(6)	37(2)
C(7)	5192(6)	3439(8)	2962(5)	22(2)
C(8)	5413(8)	3152(10)	3841(6)	30(2)
C(9)	5328(7)	2205(10)	2426(6)	31(2)
C(10)	3503(6)	6989(10)	2865(5)	27(2)
C(11)	3108(9)	6978(14)	3675(8)	55(3)
C(12)	2789(7)	6465(11)	2222(7)	38(3)
F(1)	5715(5)	9209(6)	827(4)	59(2)
F(2)	4387(6)	8750(6)	1290(5)	67(2)
F(3)	4611(5)	8333(7)	74(4)	60(2)
F(4)	6849(4)	6995(8)	533(4)	56(2)
F(5)	5715(5)	6217(8)	-248(3)	57(2)
F(6)	6257(5)	5020(7)	739(4)	60(2)
F(7)	7943(4)	7433(7)	4089(4)	47(2)
F(8)	7286(5)	5516(6)	4268(3)	42(2)
F(9)	7382(5)	6969(7)	5207(3)	56(2)
F(10)	6729(5)	9694(5)	3845(3)	43(2)
F(11)	5300(5)	9298(6)	4097(5)	64(2)
F(12)	6382(5)	9260(6)	5040(3)	53(2)
F(13)	6302(4)	2760(6)	3985(3)	38(1)
F(14)	5286(4)	4271(5)	4260(3)	38(2)
F(15)	4858(5)	2191(6)	4115(3)	44(2)
F(16)	6226(4)	1800(6)	2448(3)	38(1)
F(17)	4831(5)	1123(6)	2634(4)	47(2)
F(18)	5079(5)	2501(6)	1689(3)	47(2)
F(19)	3709(7)	7605(11)	4181(5)	104(4)
F(20)	2287(6)	7669(10)	3669(5)	90(3)
F(21)	2948(6)	5772(9)	3946(5)	81(3)
F(22)	2409(5)	5265(7)	2412(5)	66(2)
F(23)	2073(5)	7330(8)	2078(5)	69(2)
F(24)	3183(5)	6277(9)	1543(4)	69(2)

$U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Li–F4 bond could occur with very little shortening of the remaining bonds to compensate for the loss of only 0.095 units of bond valence.

The bond–valence plots in Fig. 7 suggest a

way to define the distance beyond which little or no bonding occurs between a metal ion and a ligand, a distance normally thought of as the sum of van der Waals radii. Taking the reason-

Table 15

Bond lengths (Å) and angles (°) for TlAl(OC(H)(CF₃)₂)₄

Tl-O(1)	2.805(6)	Tl-O(2)	2.855(6)
Tl-F(10)	2.967(6)	Tl-O(3)#1	2.992(6)
Tl-F(16)#1	3.045(6)	Tl-F(1)	3.090(7)
Tl-F(8)#1	3.153(6)	Tl-F(16)#2	3.242(5)
Tl-F(13)#1	3.245(6)	Tl-F(4)	3.398(7)
Tl-F(7)	3.540(6)	Tl-Al	3.684(3)
Tl-C(1)	3.733(9)	Tl-Al#1	4.105(3)
Tl-F(17)#2	4.126(7)	Tl-F(6)#1	4.143(7)
Al-O(4)	1.702(7)	Al-O(2)	1.738(6)
Al-O(1)	1.744(6)	Al-O(3)	1.757(6)
Al-Tl#3	4.105(3)	O(1)-C(1)	1.394(10)
O(1)-C(2)	2.340(12)	O(1)-C(3)	2.366(12)
O(1)-O(2)	2.583(8)	O(1)-F(2)	2.714(9)
O(1)-F(4)	2.744(8)	O(1)-F(1)	2.749(8)
O(2)-C(4)	1.394(10)	O(2)-C(6)	2.356(12)
O(2)-C(5)	2.372(11)	O(2)-F(10)	2.701(8)
O(2)-F(8)	2.738(9)	O(2)-F(7)	2.759(9)
O(3)-C(7)	1.385(10)	O(3)-C(9)	2.367(11)
O(3)-C(8)	2.373(11)	O(3)-O(4)	2.720(9)
O(3)-F(14)	2.730(8)	O(3)-F(18)	2.758(9)
O(3)-F(16)	2.760(8)	O(4)-C(10)	1.356(10)
O(4)-C(12)	2.349(12)	O(4)-C(11)	2.353(15)
O(4)-F(24)	2.656(9)	O(4)-F(21)	2.748(10)
O(4)-F(19)	2.780(11)	C(1)-C(2)	1.498(13)
C(1)-C(3)	1.511(14)	C(1)-F(6)	2.325(11)
C(1)-F(2)	2.329(11)	C(1)-F(3)	2.353(10)
C(1)-F(4)	2.362(11)	C(1)-F(1)	2.364(10)
C(1)-F(5)	2.365(10)	C(2)-F(3)	1.320(11)
C(2)-F(2)	1.339(13)	C(2)-F(1)	1.341(12)
C(3)-F(6)	1.325(12)	C(3)-F(5)	1.334(11)
C(3)-F(4)	1.344(12)	C(4)-C(5)	1.504(13)
C(4)-C(6)	1.532(13)	C(4)-F(8)	2.316(11)
C(4)-F(7)	2.351(11)	C(4)-F(11)	2.353(11)
C(4)-F(9)	2.362(10)	C(4)-F(10)	2.400(10)
C(4)-F(12)	2.405(10)	C(5)-F(9)	1.316(10)
C(5)-F(7)	1.327(12)	C(5)-F(8)	1.338(11)
C(6)-F(11)	1.334(12)	C(6)-F(12)	1.341(12)
C(6)-F(10)	1.344(11)	C(7)-C(8)	1.527(13)
C(7)-C(9)	1.530(12)	C(7)-F(18)	2.337(10)
C(7)-F(14)	2.338(10)	C(7)-F(13)	2.369(10)
C(7)-F(15)	2.374(9)	C(7)-F(16)	2.380(10)
C(7)-F(17)	2.386(10)	C(8)-F(14)	1.325(10)
C(8)-F(15)	1.332(11)	C(8)-F(13)	1.333(12)
C(9)-F(18)	1.308(11)	C(9)-F(17)	1.334(11)
C(9)-F(16)	1.339(11)	C(10)-C(11)	1.51(2)
C(10)-C(12)	1.532(13)	C(10)-F(19)	2.308(12)
C(10)-F(24)	2.360(11)	C(10)-F(21)	2.360(11)
C(10)-F(20)	2.364(11)	C(10)-F(23)	2.389(10)
C(10)-F(22)	2.394(12)	C(11)-F(21)	1.293(15)
C(11)-F(19)	1.325(15)	C(11)-F(20)	1.352(15)
C(12)-F(24)	1.322(12)	C(12)-F(23)	1.338(12)
C(12)-F(22)	1.342(12)	F(1)-F(2)	2.140(11)
F(1)-F(3)	2.144(9)	F(1)-F(4)	2.770(10)
F(1)-F(3)#4	2.873(8)	F(2)-F(3)	2.140(10)

Table 15 (continued)

F(3)-F(5)	2.680(10)	F(3)-F(1)#4	2.873(8)
F(4)-F(6)	2.150(10)	F(4)-F(5)	2.165(9)
F(4)-F(13)#1	2.813(9)	F(5)-F(6)	2.147(10)
F(6)-F(7)#3	2.789(9)	F(6)-Tl#3	4.143(7)
F(7)-F(8)	2.130(9)	F(7)-F(9)	2.146(9)
F(7)-F(6)#1	2.789(9)	F(7)-F(10)	2.828(9)
F(8)-F(9)	2.131(8)	F(8)-Tl#3	3.153(6)
F(9)-F(12)	2.666(10)	F(10)-F(11)	2.142(10)
F(10)-F(12)	2.152(8)	F(11)-F(12)	2.151(11)
F(11)-F(19)	2.823(12)	F(12)-F(15)#5	2.738(8)
F(13)-F(14)	2.144(8)	F(13)-F(15)	2.157(9)
F(13)-F(16)	2.760(8)	F(13)-F(4)#3	2.813(9)
F(13)-Tl#3	3.245(6)	F(14)-F(15)	2.139(8)
F(15)-F(17)	2.712(8)	F(15)-F(12)#5	2.738(8)
F(16)-F(18)	2.131(9)	F(16)-F(17)	2.138(9)
F(16)-Tl#3	3.045(6)	F(16)-Tl#6	3.242(5)
F(17)-F(18)	2.138(8)	F(17)-Tl#6	4.126(7)
F(19)-F(21)	2.124(13)	F(19)-F(20)	2.157(13)
F(20)-F(21)	2.124(12)	F(20)-F(23)	2.710(12)
F(21)-F(22)	2.707(11)	F(22)-F(24)	2.135(10)
F(22)-F(23)	2.148(11)	F(23)-F(24)	2.136(10)
O(1)-Tl-O(2)	54.3(2)	O(1)-Tl-F(10)	102.9(2)
O(2)-Tl-F(10)	55.3(2)	O(1)-Tl-O(3)#1	147.5(2)
O(2)-Tl-O(3)#1	128.5(2)	F(10)-Tl-O(3)#1	100.6(2)
O(1)-Tl-F(16)#1	98.3(2)	O(2)-Tl-F(16)#1	84.8(2)
F(10)-Tl-F(16)#1	102.9(2)	O(3)#1-Tl-F(16)#1	54.4(2)
O(1)-Tl-F(1)	55.4(2)	O(2)-Tl-F(1)	102.6(2)
F(10)-Tl-F(1)	119.8(2)	O(3)#1-Tl-F(1)	127.6(2)
F(16)#1-Tl-F(1)	132.7(2)	O(1)-Tl-F(8)#1	110.1(2)
O(2)-Tl-F(8)#1	162.9(2)	F(10)-Tl-F(8)#1	131.89(15)
O(3)#1-Tl-F(8)#1	68.1(2)	F(16)#1-Tl-F(8)#1	105.9(2)
F(1)-Tl-F(8)#1	60.3(2)	O(1)-Tl-F(16)#2	107.9(2)
O(2)-Tl-F(16)#2	101.7(2)	F(10)-Tl-F(16)#2	61.55(15)
O(3)#1-Tl-F(16)#2	102.9(2)	F(16)#1-Tl-F(16)#2	151.79(11)
F(1)-Tl-F(16)#2	73.2(2)	F(8)#1-Tl-F(16)#2	75.28(15)
O(1)-Tl-F(13)#1	97.5(2)	O(2)-Tl-F(13)#1	126.4(2)
F(10)-Tl-F(13)#1	150.0(2)	O(3)#1-Tl-F(13)#1	52.96(15)
F(16)#1-Tl-F(13)#1	51.92(15)	F(1)-Tl-F(13)#1	89.9(2)
F(8)#1-Tl-F(13)#1	57.3(2)	F(16)#2-Tl-F(13)#1	131.61(14)
O(1)-Tl-F(4)	51.4(2)	O(2)-Tl-F(4)	101.0(2)
F(10)-Tl-F(4)	154.3(2)	O(3)#1-Tl-F(4)	102.78(15)
F(16)#1-Tl-F(4)	82.4(2)	F(1)-Tl-F(4)	50.3(2)
F(8)#1-Tl-F(4)	68.1(2)	F(16)#2-Tl-F(4)	122.2(2)
F(13)#1-Tl-F(4)	50.04(14)	O(1)-Tl-F(7)	98.8(2)
O(2)-Tl-F(7)	49.7(2)	F(10)-Tl-F(7)	50.6(2)
O(3)#1-Tl-F(7)	79.3(2)	F(16)#1-Tl-F(7)	53.28(14)
F(1)-Tl-F(7)	152.2(2)	F(8)#1-Tl-F(7)	147.3(2)
F(16)#2-Tl-F(7)	110.82(15)	F(13)#1-Tl-F(7)	104.85(14)
F(4)-Tl-F(7)	124.3(2)	O(1)-Tl-Al	27.11(12)
O(2)-Tl-Al	27.24(12)	F(10)-Tl-Al	79.37(12)
O(3)#1-Tl-Al	144.37(12)	F(16)#1-Tl-Al	90.53(11)
F(1)-Tl-Al	79.18(12)	F(8)#1-Tl-Al	137.02(11)
F(16)#2-Tl-Al	107.90(11)	F(13)#1-Tl-Al	112.95(11)
F(4)-Tl-Al	75.38(11)	F(7)-Tl-Al	73.45(11)
O(1)-Tl-C(1)	18.5(2)	O(2)-Tl-C(1)	72.6(2)
F(10)-Tl-C(1)	117.1(2)	O(3)#1-Tl-C(1)	141.0(2)
F(16)#1-Tl-C(1)	104.7(2)	F(1)-Tl-C(1)	39.1(2)

able, if arbitrary, distance at which $s = 0.03$ as the effective limit of metal–ligand bonding leads to a bonding limit of 3.165 Å for Li–F and

3.580 for Tl–F. Since the van der Waals radius of fluorine is 1.47 Å, the metal–ion portion of these $s = 0.03$ distances are 1.70 and 2.11 Å for

Table 15 (continued)

F(8)#1-Tl-C(1)	91.6(2)	F(16)#2-Tl-C(1)	103.4(2)
F(13)#1-Tl-C(1)	88.0(2)	F(4)-Tl-C(1)	38.3(2)
F(7)-Tl-C(1)	116.7(2)	Al-Tl-C(1)	45.50(14)
O(1)-Tl-Al#1	165.07(13)	O(2)-Tl-Al#1	137.30(12)
F(10)-Tl-Al#1	91.96(12)	O(3)#1-Tl-Al#1	22.37(12)
F(16)#1-Tl-Al#1	76.31(11)	F(1)-Tl-Al#1	118.42(12)
F(8)#1-Tl-Al#1	59.43(12)	F(16)#2-Tl-Al#1	80.68(11)
F(13)#1-Tl-Al#1	68.07(11)	F(4)-Tl-Al#1	113.71(11)
F(7)-Tl-Al#1	89.12(11)	Al-Tl-Al#1	162.33(4)
C(1)-Tl-Al#1	149.14(14)	O(1)-Tl-F(17)#2	78.9(2)
O(2)-Tl-F(17)#2	76.3(2)	F(10)-Tl-F(17)#2	57.9(2)
O(3)#1-Tl-F(17)#2	133.13(14)	F(16)#1-Tl-F(17)#2	158.56(13)
F(1)-Tl-F(17)#2	62.8(2)	F(8)#1-Tl-F(17)#2	94.93(14)
F(16)#2-Tl-F(17)#2	30.87(13)	F(13)#1-Tl-F(17)#2	149.33(13)
F(4)-Tl-F(17)#2	110.76(14)	F(7)-Tl-F(17)#2	105.80(13)
Al-Tl-F(17)#2	77.27(9)	C(1)-Tl-F(17)#2	79.3(2)
Al#1-Tl-F(17)#2	111.21(9)	O(1)-Tl-F(6)#1	137.81(15)
O(2)-Tl-F(6)#1	83.70(15)	F(10)-Tl-F(6)#1	45.1(2)
O(3)#1-Tl-F(6)#1	56.22(14)	F(16)#1-Tl-F(6)#1	71.25(15)
F(1)-Tl-F(6)#1	155.2(2)	F(8)#1-Tl-F(6)#1	112.12(14)
F(16)#2-Tl-F(6)#1	82.12(15)	F(13)#1-Tl-F(6)#1	105.73(14)
F(4)-Tl-F(6)#1	152.8(2)	F(7)-Tl-F(6)#1	41.64(14)
Al-Tl-F(6)#1	110.74(10)	C(1)-Tl-F(6)#1	156.2(2)
Al#1-Tl-F(6)#1	54.11(10)	F(17)#2-Tl-F(6)#1	96.40(13)
O(4)-Al-O(2)	118.3(4)	O(4)-Al-O(1)	116.5(3)
O(2)-Al-O(1)	95.8(3)	O(4)-Al-O(3)	103.7(3)
O(2)-Al-O(3)	111.6(3)	O(1)-Al-O(3)	111.1(3)
O(4)-Al-Tl	136.0(3)	O(2)-Al-Tl	48.8(2)
O(1)-Al-Tl	47.1(2)	O(3)-Al-Tl	120.2(2)
O(4)-Al-Tl#3	142.9(3)	O(2)-Al-Tl#3	79.6(2)
O(1)-Al-Tl#3	91.3(2)	O(3)-Al-Tl#3	40.4(2)
Tl-Al-Tl#3	80.77(5)	C(1)-O(1)-Al	131.9(6)
C(1)-O(1)-C(2)	37.5(5)	Al-O(1)-C(2)	137.6(5)
C(1)-O(1)-C(3)	37.1(5)	Al-O(1)-C(3)	138.0(4)
C(2)-O(1)-C(3)	64.9(4)	C(1)-O(1)-O(2)	169.8(6)
Al-O(1)-O(2)	42.0(2)	C(2)-O(1)-O(2)	137.8(4)
C(3)-O(1)-O(2)	152.7(4)	C(1)-O(1)-F(2)	59.1(5)
Al-O(1)-F(2)	109.9(3)	C(2)-O(1)-F(2)	29.5(3)
C(3)-O(1)-F(2)	92.8(4)	O(2)-O(1)-F(2)	113.0(3)
C(1)-O(1)-F(4)	59.4(5)	Al-O(1)-F(4)	149.3(4)
C(2)-O(1)-F(4)	70.9(4)	C(3)-O(1)-F(4)	29.3(3)
O(2)-O(1)-F(4)	130.4(3)	F(2)-O(1)-F(4)	100.0(3)
C(1)-O(1)-F(1)	59.3(4)	Al-O(1)-F(1)	149.2(4)
C(2)-O(1)-F(1)	29.2(3)	C(3)-O(1)-F(1)	70.4(4)
O(2)-O(1)-F(1)	121.0(3)	F(2)-O(1)-F(1)	46.1(3)
F(4)-O(1)-F(1)	60.6(3)	C(4)-O(2)-Al	133.3(6)
C(4)-O(2)-C(6)	38.4(5)	Al-O(2)-C(6)	141.5(4)
C(4)-O(2)-C(5)	36.6(5)	Al-O(2)-C(5)	137.0(4)
C(6)-O(2)-C(5)	64.6(4)	C(4)-O(2)-O(1)	171.2(6)
Al-O(2)-O(1)	42.2(2)	C(6)-O(2)-O(1)	137.5(4)
C(5)-O(2)-O(1)	152.0(4)	C(4)-O(2)-F(10)	62.5(4)
Al-O(2)-F(10)	148.7(4)	C(6)-O(2)-F(10)	29.8(3)
C(5)-O(2)-F(10)	73.2(3)	O(1)-O(2)-F(10)	117.3(3)
C(4)-O(2)-F(8)	57.7(4)	Al-O(2)-F(8)	109.1(3)
C(6)-O(2)-F(8)	92.3(3)	C(5)-O(2)-F(8)	29.2(3)
O(1)-O(2)-F(8)	129.0(3)	F(10)-O(2)-F(8)	102.0(3)
C(4)-O(2)-F(7)	58.4(5)	Al-O(2)-F(7)	147.0(4)
C(6)-O(2)-F(7)	69.5(3)	C(5)-O(2)-F(7)	28.7(3)

Li⁺ and Tl⁺, respectively. These are remarkably close to the published van der Waals radii of lithium and thallium, which are 1.82 and 1.96

Å, respectively [68]. For Li–O and Tl–O bonds, the metal–ion portion of the $s = 0.03$ distances for Li⁺ and Tl⁺ are 1.75 and 2.25 Å. It will be

Table 15 (continued)

O(1)-O(2)-F(7)	129.9(3)	F(10)-O(2)-F(7)	62.4(2)
F(8)-O(2)-F(7)	45.6(2)	C(7)-O(3)-Al	124.7(5)
C(7)-O(3)-C(9)	37.8(5)	Al-O(3)-C(9)	147.2(4)
C(7)-O(3)-C(8)	37.5(5)	Al-O(3)-C(8)	119.4(4)
C(9)-O(3)-C(8)	65.4(4)	C(7)-O(3)-O(4)	87.6(5)
Al-O(3)-O(4)	37.4(2)	C(9)-O(3)-O(4)	114.0(4)
C(8)-O(3)-O(4)	93.9(3)	C(7)-O(3)-F(14)	58.9(4)
Al-O(3)-F(14)	91.5(3)	C(9)-O(3)-F(14)	93.0(3)
C(8)-O(3)-F(14)	29.0(3)	O(4)-O(3)-F(14)	74.0(2)
C(7)-O(3)-F(18)	57.9(4)	Al-O(3)-F(18)	125.4(3)
C(9)-O(3)-F(18)	28.3(3)	C(8)-O(3)-F(18)	91.9(3)
O(4)-O(3)-F(18)	104.1(3)	F(14)-O(3)-F(18)	116.8(3)
C(7)-O(3)-F(16)	59.6(4)	Al-O(3)-F(16)	168.3(3)
C(9)-O(3)-F(16)	29.0(3)	C(8)-O(3)-F(16)	71.0(3)
O(4)-O(3)-F(16)	142.9(3)	F(14)-O(3)-F(16)	99.5(2)
F(18)-O(3)-F(16)	45.4(2)	C(10)-O(4)-Al	143.3(6)
C(10)-O(4)-C(12)	38.2(5)	Al-O(4)-C(12)	141.6(5)
C(10)-O(4)-C(11)	37.1(5)	Al-O(4)-C(11)	146.4(5)
C(12)-O(4)-C(11)	64.9(5)	C(10)-O(4)-F(24)	62.5(5)
Al-O(4)-F(24)	112.6(4)	C(12)-O(4)-F(24)	29.8(3)
C(11)-O(4)-F(24)	94.3(4)	C(10)-O(4)-O(3)	173.8(6)
Al-O(4)-O(3)	38.9(2)	C(12)-O(4)-O(3)	135.7(4)
C(11)-O(4)-O(3)	146.7(4)	F(24)-O(4)-O(3)	111.5(3)
C(10)-O(4)-F(21)	59.2(5)	Al-O(4)-F(21)	147.0(4)
C(12)-O(4)-F(21)	71.3(4)	C(11)-O(4)-F(21)	28.0(4)
F(24)-O(4)-F(21)	99.6(3)	O(3)-O(4)-F(21)	122.5(3)
C(10)-O(4)-F(19)	55.8(5)	Al-O(4)-F(19)	118.1(4)
C(12)-O(4)-F(19)	90.7(4)	C(11)-O(4)-F(19)	28.4(4)
F(24)-O(4)-F(19)	118.2(3)	O(3)-O(4)-F(19)	130.1(3)
F(21)-O(4)-F(19)	45.2(3)	O(1)-C(1)-C(2)	108.0(7)
O(1)-C(1)-C(3)	109.0(8)	C(2)-C(1)-C(3)	114.1(9)
O(1)-C(1)-F(6)	92.3(6)	C(2)-C(1)-F(6)	146.4(7)
C(3)-C(1)-F(6)	32.4(5)	O(1)-C(1)-F(2)	90.0(5)
C(2)-C(1)-F(2)	32.6(5)	C(3)-C(1)-F(2)	146.8(7)
F(6)-C(1)-F(2)	177.6(5)	O(1)-C(1)-F(3)	139.1(6)
C(2)-C(1)-F(3)	31.1(5)	C(3)-C(1)-F(3)	96.2(6)
F(6)-C(1)-F(3)	123.7(5)	F(2)-C(1)-F(3)	54.4(3)
O(1)-C(1)-F(4)	90.1(6)	C(2)-C(1)-F(4)	97.9(7)
C(3)-C(1)-F(4)	32.0(5)	F(6)-C(1)-F(4)	54.6(3)
F(2)-C(1)-F(4)	126.0(5)	F(3)-C(1)-F(4)	95.7(4)
O(1)-C(1)-F(1)	90.2(5)	C(2)-C(1)-F(1)	31.6(5)
C(3)-C(1)-F(1)	97.5(6)	F(6)-C(1)-F(1)	126.3(5)
F(2)-C(1)-F(1)	54.3(3)	F(3)-C(1)-F(1)	54.1(3)
F(4)-C(1)-F(1)	71.8(4)	O(1)-C(1)-F(5)	140.5(7)
C(2)-C(1)-F(5)	95.1(6)	C(3)-C(1)-F(5)	31.5(5)
F(6)-C(1)-F(5)	54.5(3)	F(2)-C(1)-F(5)	123.6(5)
F(3)-C(1)-F(5)	69.2(3)	F(4)-C(1)-F(5)	54.5(3)
F(1)-C(1)-F(5)	93.7(4)	O(1)-C(1)-T1	39.6(4)
C(2)-C(1)-T1	82.9(5)	C(3)-C(1)-T1	93.1(6)
F(6)-C(1)-T1	97.7(3)	F(2)-C(1)-T1	84.4(3)
F(3)-C(1)-T1	109.6(3)	F(4)-C(1)-T1	63.1(3)
F(1)-C(1)-T1	55.6(2)	F(5)-C(1)-T1	116.7(4)
F(3)-C(2)-F(2)	107.2(10)	F(3)-C(2)-F(1)	107.4(8)
F(2)-C(2)-F(1)	106.0(9)	F(3)-C(2)-C(1)	113.0(9)
F(2)-C(2)-C(1)	110.2(8)	F(1)-C(2)-C(1)	112.6(9)
F(3)-C(2)-O(1)	147.5(8)	F(2)-C(2)-O(1)	90.9(6)
F(1)-C(2)-O(1)	92.6(6)	C(1)-C(2)-O(1)	34.5(4)
F(6)-C(3)-F(5)	107.7(9)	F(6)-C(3)-F(4)	107.3(8)

interesting to see if the $s = 0.03$ limit correlates with van der Waals radii for other metal ions because, if it does, the bond–valence method

could be used to determine unknown metal–ion van der Waals radii.

Table 15 (continued)

F(5)-C(3)-F(4)	107.9(8)	F(6)-C(3)-C(1)	110.0(8)
F(5)-C(3)-C(1)	112.3(8)	F(4)-C(3)-C(1)	111.5(9)
F(6)-C(3)-O(1)	92.3(6)	F(5)-C(3)-O(1)	146.1(8)
F(4)-C(3)-O(1)	91.1(6)	C(1)-C(3)-O(1)	33.8(4)
O(2)-C(4)-C(5)	109.8(7)	O(2)-C(4)-C(6)	107.2(7)
C(5)-C(4)-C(6)	112.5(8)	O(2)-C(4)-F(8)	91.7(5)
C(5)-C(4)-F(8)	33.1(4)	C(6)-C(4)-F(8)	145.6(7)
O(2)-C(4)-F(7)	91.2(5)	C(5)-C(4)-F(7)	31.5(4)
C(6)-C(4)-F(7)	95.8(6)	F(8)-C(4)-F(7)	54.3(3)
O(2)-C(4)-F(11)	93.4(6)	C(5)-C(4)-F(11)	144.1(7)
C(6)-C(4)-F(11)	32.2(5)	F(8)-C(4)-F(11)	174.9(5)
F(7)-C(4)-F(11)	125.9(5)	O(2)-C(4)-F(9)	140.5(6)
C(5)-C(4)-F(9)	30.7(4)	C(6)-C(4)-F(9)	95.9(6)
F(8)-C(4)-F(9)	54.2(3)	F(7)-C(4)-F(9)	54.2(3)
F(11)-C(4)-F(9)	121.2(4)	O(2)-C(4)-F(10)	86.5(5)
C(5)-C(4)-F(10)	99.6(6)	C(6)-C(4)-F(10)	31.1(5)
F(8)-C(4)-F(10)	127.3(5)	F(7)-C(4)-F(10)	73.1(4)
F(11)-C(4)-F(10)	53.6(3)	F(9)-C(4)-F(10)	98.7(4)
O(2)-C(4)-F(12)	137.5(6)	C(5)-C(4)-F(12)	91.9(6)
C(6)-C(4)-F(12)	30.8(5)	F(8)-C(4)-F(12)	122.0(4)
F(7)-C(4)-F(12)	89.4(4)	F(11)-C(4)-F(12)	53.7(3)
F(9)-C(4)-F(12)	68.0(3)	F(10)-C(4)-F(12)	53.2(3)
F(9)-C(5)-F(7)	108.6(9)	F(9)-C(5)-F(8)	106.8(8)
F(7)-C(5)-F(8)	106.1(8)	F(9)-C(5)-C(4)	113.6(8)
F(7)-C(5)-C(4)	112.2(8)	F(8)-C(5)-C(4)	109.0(9)
F(9)-C(5)-O(2)	147.2(8)	F(7)-C(5)-O(2)	92.1(6)
F(8)-C(5)-O(2)	90.7(6)	C(4)-C(5)-O(2)	33.6(4)
F(11)-C(6)-F(12)	107.1(9)	F(11)-C(6)-F(10)	106.2(9)
F(12)-C(6)-F(10)	106.6(8)	F(11)-C(6)-C(4)	110.2(9)
F(12)-C(6)-C(4)	113.5(8)	F(10)-C(6)-C(4)	112.9(8)
F(11)-C(6)-O(2)	94.9(7)	F(12)-C(6)-O(2)	147.3(8)
F(10)-C(6)-O(2)	89.5(6)	C(4)-C(6)-O(2)	34.4(4)
O(3)-C(7)-C(8)	109.0(7)	O(3)-C(7)-C(9)	108.5(7)
C(8)-C(7)-C(9)	113.9(7)	O(3)-C(7)-F(18)	92.0(5)
C(8)-C(7)-F(18)	145.4(6)	C(9)-C(7)-F(18)	31.6(4)
O(3)-C(7)-F(14)	90.6(5)	C(8)-C(7)-F(14)	32.2(4)
C(9)-C(7)-F(14)	146.1(6)	F(18)-C(7)-F(14)	177.2(5)
O(3)-C(7)-F(13)	92.2(5)	C(8)-C(7)-F(13)	31.5(5)
C(9)-C(7)-F(13)	96.2(6)	F(18)-C(7)-F(13)	124.6(4)
F(14)-C(7)-F(13)	54.2(3)	O(3)-C(7)-F(15)	140.3(6)
C(8)-C(7)-F(15)	31.3(4)	C(9)-C(7)-F(15)	96.8(6)
F(18)-C(7)-F(15)	123.2(4)	F(14)-C(7)-F(15)	54.0(3)
F(13)-C(7)-F(15)	54.1(3)	O(3)-C(7)-F(16)	90.3(5)
C(8)-C(7)-F(16)	97.8(6)	C(9)-C(7)-F(16)	31.5(4)
F(18)-C(7)-F(16)	53.7(3)	F(14)-C(7)-F(16)	125.2(4)
F(13)-C(7)-F(16)	71.1(3)	F(15)-C(7)-F(16)	96.4(4)
O(3)-C(7)-F(17)	139.5(6)	C(8)-C(7)-F(17)	94.6(5)
C(9)-C(7)-F(17)	31.1(4)	F(18)-C(7)-F(17)	53.8(3)
F(14)-C(7)-F(17)	123.3(4)	F(13)-C(7)-F(17)	91.6(4)
F(15)-C(7)-F(17)	69.5(3)	F(16)-C(7)-F(17)	53.3(3)
F(14)-C(8)-F(15)	107.2(7)	F(14)-C(8)-F(13)	107.5(8)
F(15)-C(8)-F(13)	108.1(8)	F(14)-C(8)-C(7)	110.0(8)
F(15)-C(8)-C(7)	112.1(8)	F(13)-C(8)-C(7)	111.7(8)
F(14)-C(8)-O(3)	90.6(5)	F(15)-C(8)-O(3)	145.6(7)
F(13)-C(8)-O(3)	93.4(6)	C(7)-C(8)-O(3)	33.5(4)
F(18)-C(9)-F(17)	108.1(8)	F(18)-C(9)-F(16)	107.2(8)
F(17)-C(9)-F(16)	106.2(8)	F(18)-C(9)-C(7)	110.6(8)
F(17)-C(9)-C(7)	112.6(8)	F(16)-C(9)-C(7)	111.9(8)

4.3. The strength of Li–F(C) bonds and the design of improved weakly coordinating anions

The four Li–F(C) bonds in LiAl(HFPP)₄,

which provide more than half of the sum of lithium bond valences, are clearly very important in the overall stability of this compound. The calculated (6-31G^{*}) Li–F(C) bond dissoci-

Table 15 (continued)

F(18)-C(9)-O(3)	92.7(6)	F(17)-C(9)-O(3)	146.2(7)
F(16)-C(9)-O(3)	92.0(6)	C(7)-C(9)-O(3)	33.7(4)
O(4)-C(10)-C(11)	110.1(9)	O(4)-C(10)-C(12)	108.7(8)
C(11)-C(10)-C(12)	111.8(9)	O(4)-C(10)-F(19)	95.2(6)
C(11)-C(10)-F(19)	32.9(6)	C(12)-C(10)-F(19)	144.3(7)
O(4)-C(10)-F(24)	86.9(6)	C(11)-C(10)-F(24)	142.6(8)
C(12)-C(10)-F(24)	31.5(5)	F(19)-C(10)-F(24)	175.6(5)
O(4)-C(10)-F(21)	91.3(6)	C(11)-C(10)-F(21)	30.0(6)
C(12)-C(10)-F(21)	98.1(6)	F(19)-C(10)-F(21)	54.1(4)
F(24)-C(10)-F(21)	122.0(5)	O(4)-C(10)-F(20)	142.2(7)
C(11)-C(10)-F(20)	32.3(6)	C(12)-C(10)-F(20)	91.3(6)
F(19)-C(10)-F(20)	55.0(4)	F(24)-C(10)-F(20)	121.5(5)
F(21)-C(10)-F(20)	53.5(4)	O(4)-C(10)-F(23)	138.9(7)
C(11)-C(10)-F(23)	98.8(7)	C(12)-C(10)-F(23)	31.1(5)
F(19)-C(10)-F(23)	123.7(5)	F(24)-C(10)-F(23)	53.4(3)
F(21)-C(10)-F(23)	100.8(4)	F(20)-C(10)-F(23)	69.5(4)
O(4)-C(10)-F(22)	96.7(6)	C(11)-C(10)-F(22)	90.8(7)
C(12)-C(10)-F(22)	31.2(5)	F(19)-C(10)-F(22)	122.4(5)
F(24)-C(10)-F(22)	53.4(3)	F(21)-C(10)-F(22)	69.4(4)
F(20)-C(10)-F(22)	84.1(4)	F(23)-C(10)-F(22)	53.4(3)
F(21)-C(11)-F(19)	108.4(12)	F(21)-C(11)-F(20)	106.8(11)
F(19)-C(11)-F(20)	107.4(12)	F(21)-C(11)-C(10)	114.3(12)
F(19)-C(11)-C(10)	108.7(10)	F(20)-C(11)-C(10)	111.1(10)
F(21)-C(11)-O(4)	93.2(9)	F(19)-C(11)-O(4)	94.0(8)
F(20)-C(11)-O(4)	143.7(9)	C(10)-C(11)-O(4)	32.8(5)
F(24)-C(12)-F(23)	106.8(9)	F(24)-C(12)-F(22)	106.5(9)
F(23)-C(12)-F(22)	106.5(8)	F(24)-C(12)-C(10)	111.3(8)
F(23)-C(12)-C(10)	112.6(9)	F(22)-C(12)-C(10)	112.6(9)
F(24)-C(12)-O(4)	88.1(6)	F(23)-C(12)-O(4)	144.7(8)
F(22)-C(12)-O(4)	99.2(7)	C(10)-C(12)-O(4)	33.2(4)
C(2)-F(1)-F(2)	36.9(6)	C(2)-F(1)-F(3)	36.0(5)
F(2)-F(1)-F(3)	59.9(3)	C(2)-F(1)-C(1)	35.8(5)
F(2)-F(1)-C(1)	62.0(3)	F(3)-F(1)-C(1)	62.7(3)
C(2)-F(1)-O(1)	58.2(5)	F(2)-F(1)-O(1)	66.1(3)
F(3)-F(1)-O(1)	91.3(3)	C(1)-F(1)-O(1)	30.5(2)
C(2)-F(1)-F(4)	84.8(6)	F(2)-F(1)-F(4)	116.1(3)
F(3)-F(1)-F(4)	89.7(3)	C(1)-F(1)-F(4)	54.1(3)
O(1)-F(1)-F(4)	59.6(2)	C(2)-F(1)-F(3)#4	116.4(6)
F(2)-F(1)-F(3)#4	104.6(3)	F(3)-F(1)-F(3)#4	86.1(3)
C(1)-F(1)-F(3)#4	148.7(4)	O(1)-F(1)-F(3)#4	170.2(4)
F(4)-F(1)-F(3)#4	129.7(3)	C(2)-F(1)-T1	114.7(5)
F(2)-F(1)-T1	105.5(3)	F(3)-F(1)-T1	148.0(3)
C(1)-F(1)-T1	85.3(3)	O(1)-F(1)-T1	57.1(2)
F(4)-F(1)-T1	70.6(2)	F(3)#4-F(1)-T1	126.0(2)
C(2)-F(2)-F(3)	36.1(5)	C(2)-F(2)-F(1)	37.0(5)
F(3)-F(2)-F(1)	60.1(3)	C(2)-F(2)-C(1)	37.1(5)
F(3)-F(2)-C(1)	63.4(3)	F(1)-F(2)-C(1)	63.7(4)
C(2)-F(2)-O(1)	59.6(5)	F(3)-F(2)-O(1)	92.4(3)
F(1)-F(2)-O(1)	67.8(3)	C(1)-F(2)-O(1)	30.9(3)
C(2)-F(3)-F(2)	36.7(6)	C(2)-F(3)-F(1)	36.6(5)
F(2)-F(3)-F(1)	59.9(3)	C(2)-F(3)-C(1)	35.9(5)
F(2)-F(3)-C(1)	62.2(3)	F(1)-F(3)-C(1)	63.2(3)
C(2)-F(3)-F(5)	86.3(6)	F(2)-F(3)-F(5)	117.8(3)
F(1)-F(3)-F(5)	90.6(3)	C(1)-F(3)-F(5)	55.6(3)
C(2)-F(3)-F(1)#4	124.3(6)	F(2)-F(3)-F(1)#4	108.7(4)
F(1)-F(3)-F(1)#4	93.9(3)	C(1)-F(3)-F(1)#4	157.1(4)
F(5)-F(3)-F(1)#4	128.2(3)	C(3)-F(4)-F(6)	36.0(5)
C(3)-F(4)-F(5)	35.9(5)	F(6)-F(4)-F(5)	59.7(3)

ation energy for the $[\text{H}_3\text{CF-Li}]^+$ complex is 35 kcal mol⁻¹ [54], in reasonable agreement with the experimental value of 31 kcal mol⁻¹ [73].

The Li-F(C) bond energies in $\text{LiAl}(\text{HFPP})_4$ are undoubtedly weaker than this for two reasons. First, the C-F bond of a trifluoromethyl group

Table 15 (continued)

C(3)-F(4)-C(1)	36.5(6)	F(6)-F(4)-C(1)	61.8(3)
F(5)-F(4)-C(1)	62.8(3)	C(3)-F(4)-O(1)	59.6(5)
F(6)-F(4)-O(1)	67.4(3)	F(5)-F(4)-O(1)	91.9(3)
C(1)-F(4)-O(1)	30.5(2)	C(3)-F(4)-F(1)	84.8(6)
F(6)-F(4)-F(1)	115.9(3)	F(5)-F(4)-F(1)	87.9(3)
C(1)-F(4)-F(1)	54.2(3)	O(1)-F(4)-F(1)	59.8(2)
C(3)-F(4)-F(13)#1	158.8(7)	F(6)-F(4)-F(13)#1	124.3(4)
F(5)-F(4)-F(13)#1	157.4(3)	C(1)-F(4)-F(13)#1	139.8(4)
O(1)-F(4)-F(13)#1	110.3(3)	F(1)-F(4)-F(13)#1	106.7(3)
C(3)-F(4)-T1	112.5(6)	F(6)-F(4)-T1	112.2(3)
F(5)-F(4)-T1	139.8(3)	C(1)-F(4)-T1	78.5(3)
O(1)-F(4)-T1	53.1(2)	F(1)-F(4)-T1	59.1(2)
F(13)#1-F(4)-T1	62.2(2)	C(3)-F(5)-F(6)	36.0(6)
C(3)-F(5)-F(4)	36.2(5)	F(6)-F(5)-F(4)	59.8(3)
C(3)-F(5)-C(1)	36.2(5)	F(6)-F(5)-C(1)	61.8(3)
F(4)-F(5)-C(1)	62.7(3)	C(3)-F(5)-F(3)	87.0(6)
F(6)-F(5)-F(3)	116.9(3)	F(4)-F(5)-F(3)	91.7(3)
C(1)-F(5)-F(3)	55.2(3)	C(3)-F(6)-F(5)	36.3(5)
C(3)-F(6)-F(4)	36.7(5)	F(5)-F(6)-F(4)	60.5(3)
C(3)-F(6)-C(1)	37.7(5)	F(5)-F(6)-C(1)	63.7(3)
F(4)-F(6)-C(1)	63.6(3)	C(3)-F(6)-O(1)	59.0(5)
F(5)-F(6)-O(1)	91.9(3)	F(4)-F(6)-O(1)	66.6(3)
C(1)-F(6)-O(1)	30.3(3)	C(3)-F(6)-F(7)#3	164.3(7)
F(5)-F(6)-F(7)#3	134.8(4)	F(4)-F(6)-F(7)#3	132.3(4)
C(1)-F(6)-F(7)#3	157.9(4)	O(1)-F(6)-F(7)#3	133.2(3)
C(3)-F(6)-T1#3	127.5(6)	F(5)-F(6)-T1#3	161.5(3)
F(4)-F(6)-T1#3	101.0(3)	C(1)-F(6)-T1#3	108.7(3)
O(1)-F(6)-T1#3	78.5(2)	F(7)#3-F(6)-T1#3	57.5(2)
C(5)-F(7)-F(8)	37.1(5)	C(5)-F(7)-F(9)	35.5(5)
F(8)-F(7)-F(9)	59.8(3)	C(5)-F(7)-C(4)	36.3(5)
F(8)-F(7)-C(4)	62.0(3)	F(9)-F(7)-C(4)	63.2(3)
C(5)-F(7)-O(2)	59.2(5)	F(8)-F(7)-O(2)	66.7(3)
F(9)-F(7)-O(2)	91.9(3)	C(4)-F(7)-O(2)	30.3(2)
C(5)-F(7)-F(6)#1	131.7(6)	F(8)-F(7)-F(6)#1	165.5(4)
F(9)-F(7)-F(6)#1	105.8(3)	C(4)-F(7)-F(6)#1	114.7(4)
O(2)-F(7)-F(6)#1	118.5(3)	C(5)-F(7)-F(10)	85.9(5)
F(8)-F(7)-F(10)	116.2(3)	F(9)-F(7)-F(10)	92.1(3)
C(4)-F(7)-F(10)	54.3(3)	O(2)-F(7)-F(10)	57.8(2)
F(6)#1-F(7)-F(10)	63.0(2)	C(5)-F(7)-T1	111.1(5)
F(8)-F(7)-T1	110.8(3)	F(9)-F(7)-T1	138.9(3)
C(4)-F(7)-T1	77.1(3)	O(2)-F(7)-T1	52.1(2)
F(6)#1-F(7)-T1	80.8(2)	F(10)-F(7)-T1	54.1(2)
C(5)-F(8)-F(7)	36.8(5)	C(5)-F(8)-F(9)	36.2(5)
F(7)-F(8)-F(9)	60.5(3)	C(5)-F(8)-C(4)	37.9(6)
F(7)-F(8)-C(4)	63.7(3)	F(9)-F(8)-C(4)	64.0(3)
C(5)-F(8)-O(2)	60.0(5)	F(7)-F(8)-O(2)	67.7(3)
F(9)-F(8)-O(2)	92.8(3)	C(4)-F(8)-O(2)	30.6(2)
C(5)-F(8)-T1#3	134.2(5)	F(7)-F(8)-T1#3	102.6(3)
F(9)-F(8)-T1#3	160.1(4)	C(4)-F(8)-T1#3	120.1(3)
O(2)-F(8)-T1#3	89.5(2)	C(5)-F(9)-F(8)	36.9(5)
C(5)-F(9)-F(7)	35.9(5)	F(8)-F(9)-F(7)	59.7(3)
C(5)-F(9)-C(4)	35.7(5)	F(8)-F(9)-C(4)	61.8(3)
F(7)-F(9)-C(4)	62.7(3)	C(5)-F(9)-F(12)	85.4(6)
F(8)-F(9)-F(12)	118.3(3)	F(7)-F(9)-F(12)	87.4(3)
C(4)-F(9)-F(12)	56.8(3)	C(6)-F(10)-F(11)	36.7(5)
C(6)-F(10)-F(12)	36.7(5)	F(11)-F(10)-F(12)	60.1(3)
C(6)-F(10)-C(4)	36.0(5)	F(11)-F(10)-C(4)	62.1(3)
F(12)-F(10)-C(4)	63.5(3)	C(6)-F(10)-O(2)	60.7(5)

is probably a weaker donor than the C–F bond of a monofluoromethyl group. Second, a Li–F(C) bond to a bare Li⁺ ion is undoubtedly

stronger than any given Li–F(C) bond to a Li⁺ ion already coordinated to five other (albeit weak) ligands.

Table 15 (continued)

F(11)-F(10)-O(2)	69.7(3)	F(12)-F(10)-O(2)	93.6(3)
C(4)-F(10)-O(2)	31.0(2)	C(6)-F(10)-F(7)	80.9(5)
F(11)-F(10)-F(7)	114.2(3)	F(12)-F(10)-F(7)	83.2(3)
C(4)-F(10)-F(7)	52.7(3)	O(2)-F(10)-F(7)	59.8(2)
C(6)-F(10)-T1	120.7(6)	F(11)-F(10)-T1	113.3(3)
F(12)-F(10)-T1	152.1(3)	C(4)-F(10)-T1	89.1(3)
O(2)-F(10)-T1	60.3(2)	F(7)-F(10)-T1	75.3(2)
C(6)-F(11)-F(10)	37.1(5)	C(6)-F(11)-F(12)	36.6(5)
F(10)-F(11)-F(12)	60.2(3)	C(6)-F(11)-C(4)	37.7(5)
F(10)-F(11)-C(4)	64.3(3)	F(12)-F(11)-C(4)	64.4(3)
C(6)-F(11)-O(2)	56.8(5)	F(10)-F(11)-O(2)	64.6(3)
F(12)-F(11)-O(2)	90.8(3)	C(4)-F(11)-O(2)	29.7(2)
C(6)-F(11)-F(19)	124.9(6)	F(10)-F(11)-F(19)	153.4(4)
F(12)-F(11)-F(19)	119.7(4)	C(4)-F(11)-F(19)	91.0(4)
O(2)-F(11)-F(19)	89.1(3)	C(6)-F(12)-F(11)	36.4(5)
C(6)-F(12)-F(10)	36.8(5)	F(11)-F(12)-F(10)	59.7(3)
C(6)-F(12)-C(4)	35.8(5)	F(11)-F(12)-C(4)	61.9(3)
F(10)-F(12)-C(4)	63.3(3)	C(6)-F(12)-F(9)	88.2(5)
F(11)-F(12)-F(9)	116.6(3)	F(10)-F(12)-F(9)	96.6(3)
C(4)-F(12)-F(9)	55.2(3)	C(6)-F(12)-F(15)#5	105.2(6)
F(11)-F(12)-F(15)#5	86.5(3)	F(10)-F(12)-F(15)#5	141.7(4)
C(4)-F(12)-F(15)#5	86.0(3)	F(9)-F(12)-F(15)#5	82.3(3)
C(8)-F(13)-F(14)	36.1(5)	C(8)-F(13)-F(15)	35.9(5)
F(14)-F(13)-F(15)	59.6(3)	C(8)-F(13)-C(7)	36.8(5)
F(14)-F(13)-C(7)	62.2(3)	F(15)-F(13)-C(7)	63.1(3)
C(8)-F(13)-F(16)	86.7(5)	F(14)-F(13)-F(16)	116.8(3)
F(15)-F(13)-F(16)	91.4(3)	C(7)-F(13)-F(16)	54.7(3)
C(8)-F(13)-O(3)	58.1(5)	F(14)-F(13)-O(3)	65.7(2)
F(15)-F(13)-O(3)	90.8(3)	C(7)-F(13)-O(3)	29.7(3)
F(16)-F(13)-O(3)	59.6(2)	C(8)-F(13)-F(4)#3	173.7(6)
F(14)-F(13)-F(4)#3	139.1(3)	F(15)-F(13)-F(4)#3	141.7(3)
C(7)-F(13)-F(4)#3	149.3(3)	F(16)-F(13)-F(4)#3	99.5(3)
O(3)-F(13)-F(4)#3	126.3(3)	C(8)-F(13)-T1#3	116.9(5)
F(14)-F(13)-T1#3	113.4(3)	F(15)-F(13)-T1#3	145.5(3)
C(7)-F(13)-T1#3	83.5(3)	F(16)-F(13)-T1#3	60.3(2)
O(3)-F(13)-T1#3	58.9(2)	F(4)#3-F(13)-T1#3	67.8(2)
C(8)-F(14)-F(15)	36.5(5)	C(8)-F(14)-F(13)	36.4(5)
F(15)-F(14)-F(13)	60.5(3)	C(8)-F(14)-C(7)	37.9(5)
F(15)-F(14)-C(7)	63.9(3)	F(13)-F(14)-C(7)	63.6(3)
C(8)-F(14)-O(3)	60.3(5)	F(15)-F(14)-O(3)	92.9(3)
F(13)-F(14)-O(3)	68.6(2)	C(7)-F(14)-O(3)	30.5(3)
C(8)-F(15)-F(14)	36.3(4)	C(8)-F(15)-F(13)	36.0(5)
F(14)-F(15)-F(13)	59.9(3)	C(8)-F(15)-C(7)	36.6(5)
F(14)-F(15)-C(7)	62.2(3)	F(13)-F(15)-C(7)	62.8(3)
C(8)-F(15)-F(17)	85.8(5)	F(14)-F(15)-F(17)	117.5(3)
F(13)-F(15)-F(17)	88.1(3)	C(7)-F(15)-F(17)	55.5(3)
C(8)-F(15)-F(12)#5	164.9(6)	F(14)-F(15)-F(12)#5	128.6(3)
F(13)-F(15)-F(12)#5	146.9(4)	C(7)-F(15)-F(12)#5	149.8(4)
F(17)-F(15)-F(12)#5	107.9(3)	C(9)-F(16)-F(18)	35.9(5)
C(9)-F(16)-F(17)	36.8(5)	F(18)-F(16)-F(17)	60.1(3)
C(9)-F(16)-C(7)	36.6(5)	F(18)-F(16)-C(7)	62.1(3)
F(17)-F(16)-C(7)	63.5(3)	C(9)-F(16)-F(13)	84.7(5)
F(18)-F(16)-F(13)	116.3(3)	F(17)-F(16)-F(13)	87.2(3)
C(7)-F(16)-F(13)	54.3(3)	C(9)-F(16)-O(3)	59.0(5)
F(18)-F(16)-O(3)	67.2(3)	F(17)-F(16)-O(3)	92.2(3)
C(7)-F(16)-O(3)	30.1(2)	F(13)-F(16)-O(3)	60.7(2)
C(9)-F(16)-T1#3	120.8(5)	F(18)-F(16)-T1#3	115.7(3)
F(17)-F(16)-T1#3	150.1(3)	C(7)-F(16)-T1#3	87.9(3)

This naturally leads to the following question: in order to optimize the Lewis acidity (a thermodynamic property) and/or the elec-

trophilicity (a kinetic property) of a metal ion, is it better to have a greater number of weak M-F(C) bonds or fewer but relatively stronger

Table 15 (continued)

F(13)-F(16)-Tl#3	67.8(2)	O(3)-F(16)-Tl#3	61.8(2)
C(9)-F(16)-Tl#6	132.1(5)	F(18)-F(16)-Tl#6	122.3(3)
F(17)-F(16)-Tl#6	98.1(2)	C(7)-F(16)-Tl#6	157.1(3)
F(13)-F(16)-Tl#6	114.8(2)	O(3)-F(16)-Tl#6	168.7(3)
Tl#3-F(16)-Tl#6	107.1(2)	C(9)-F(17)-F(16)	37.0(5)
C(9)-F(17)-F(18)	35.6(5)	F(16)-F(17)-F(18)	59.8(3)
C(9)-F(17)-C(7)	36.3(5)	F(16)-F(17)-C(7)	63.2(3)
F(18)-F(17)-C(7)	61.9(3)	C(9)-F(17)-F(15)	87.6(5)
F(16)-F(17)-F(15)	93.1(3)	F(18)-F(17)-F(15)	116.9(3)
C(7)-F(17)-F(15)	55.1(3)	C(9)-F(17)-Tl#6	86.5(5)
F(16)-F(17)-Tl#6	51.1(2)	F(18)-F(17)-Tl#6	92.7(3)
C(7)-F(17)-Tl#6	112.9(3)	F(15)-F(17)-Tl#6	113.3(2)
C(9)-F(18)-F(16)	36.9(5)	C(9)-F(18)-F(17)	36.4(5)
F(16)-F(18)-F(17)	60.1(3)	C(9)-F(18)-C(7)	37.8(5)
F(16)-F(18)-C(7)	64.2(3)	F(17)-F(18)-C(7)	64.2(3)
C(9)-F(18)-O(3)	59.0(5)	F(16)-F(18)-O(3)	67.4(2)
F(17)-F(18)-O(3)	92.2(3)	C(7)-F(18)-O(3)	30.1(2)
C(11)-F(19)-F(21)	35.3(7)	C(11)-F(19)-F(20)	36.7(7)
F(21)-F(19)-F(20)	59.5(4)	C(11)-F(19)-C(10)	38.4(6)
F(21)-F(19)-C(10)	64.2(4)	F(20)-F(19)-C(10)	63.8(4)
C(11)-F(19)-O(4)	57.6(7)	F(21)-F(19)-O(4)	66.6(4)
F(20)-F(19)-O(4)	90.5(4)	C(10)-F(19)-O(4)	29.1(3)
C(11)-F(19)-F(11)	136.9(7)	F(21)-F(19)-F(11)	153.0(5)
F(20)-F(19)-F(11)	134.6(5)	C(10)-F(19)-F(11)	99.3(4)
O(4)-F(19)-F(11)	88.6(3)	C(11)-F(20)-F(21)	35.7(6)
C(11)-F(20)-F(19)	35.9(7)	F(21)-F(20)-F(19)	59.5(5)
C(11)-F(20)-C(10)	36.7(6)	F(21)-F(20)-C(10)	63.2(4)
F(19)-F(20)-C(10)	61.2(4)	C(11)-F(20)-F(23)	89.5(7)
F(21)-F(20)-F(23)	97.6(4)	F(19)-F(20)-F(23)	116.2(4)
C(10)-F(20)-F(23)	55.7(3)	C(11)-F(21)-F(19)	36.3(7)
C(11)-F(21)-F(20)	37.5(7)	F(19)-F(21)-F(20)	61.0(5)
C(11)-F(21)-C(10)	35.8(7)	F(19)-F(21)-C(10)	61.7(4)
F(20)-F(21)-C(10)	63.4(4)	C(11)-F(21)-F(22)	82.8(8)
F(19)-F(21)-F(22)	116.6(4)	F(20)-F(21)-F(22)	81.6(4)
C(10)-F(21)-F(22)	55.9(3)	C(11)-F(21)-O(4)	58.8(7)
F(19)-F(21)-O(4)	68.2(3)	F(20)-F(21)-O(4)	92.1(3)
C(10)-F(21)-O(4)	29.6(3)	F(22)-F(21)-O(4)	63.9(3)
C(12)-F(22)-F(24)	36.4(5)	C(12)-F(22)-F(23)	36.7(5)
F(24)-F(22)-F(23)	59.8(4)	C(12)-F(22)-C(10)	36.2(5)
F(24)-F(22)-C(10)	62.5(3)	F(23)-F(22)-C(10)	63.2(3)
C(12)-F(22)-F(21)	88.4(6)	F(24)-F(22)-F(21)	116.5(4)
F(23)-F(22)-F(21)	97.2(4)	C(10)-F(22)-F(21)	54.7(3)
C(12)-F(22)-O(4)	53.5(5)	F(24)-F(22)-O(4)	61.8(3)
F(23)-F(22)-O(4)	87.7(3)	C(10)-F(22)-O(4)	27.8(3)
F(21)-F(22)-O(4)	58.8(3)	C(12)-F(23)-F(24)	36.3(6)
C(12)-F(23)-F(22)	36.8(5)	F(24)-F(23)-F(22)	59.8(4)
C(12)-F(23)-C(10)	36.3(6)	F(24)-F(23)-C(10)	62.6(3)
F(22)-F(23)-C(10)	63.4(3)	C(12)-F(23)-F(20)	81.8(6)
F(24)-F(23)-F(20)	116.0(4)	F(22)-F(23)-F(20)	81.1(4)
C(10)-F(23)-F(20)	54.8(3)	C(12)-F(24)-F(22)	37.1(6)
C(12)-F(24)-F(23)	36.8(5)	F(22)-F(24)-F(23)	60.4(4)
C(12)-F(24)-C(10)	37.2(5)	F(22)-F(24)-C(10)	64.1(4)
F(23)-F(24)-C(10)	64.0(3)	C(12)-F(24)-O(4)	62.1(5)
F(22)-F(24)-O(4)	73.1(3)	F(23)-F(24)-O(4)	94.1(3)
C(10)-F(24)-O(4)	30.6(3)		

Symmetry transformations used to generate equivalent atoms: #1 $-x+3/2, y+1/2, -z+1/2$; #2 $x, y+1, z$; #3 $-x+3/2, y-1/2, -z+1/2$; #4 $-x+1, -y+2, -z$; #5 $-x+1, -y+1, -z+1$; #6 $x, y-1, z$.

M–F(C) bonds? For example, the compound $\text{LiAl}(\text{OC}(\text{CH}_3)_2(\text{CF}_3))_4$, which has not yet been prepared, might contain a four-coordinate Li^+

ion with a LiO_2F_2 coordination unit. If this is so, will $\text{LiAl}(\text{OC}(\text{CH}_3)_2(\text{CF}_3))_4$ be a more active or less active catalyst than

Table 16
Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{TlAl}(\text{OC}(\text{H})(\text{CF}_3)_2)_4$

	U11	U22	U33	U23	U13	U12
Tl	24(1)	28(1)	35(1)	4(1)	1(1)	-3(1)
Al	20(1)	18(1)	20(1)	5(1)	-2(1)	0(1)
O(1)	32(4)	25(3)	24(3)	9(3)	-9(3)	-8(3)
O(2)	27(4)	32(3)	21(3)	1(3)	-6(3)	-6(3)
O(3)	23(3)	20(3)	33(3)	10(3)	7(3)	7(3)
O(4)	17(3)	28(3)	59(4)	13(4)	-5(3)	3(3)
C(1)	29(5)	22(5)	27(5)	5(4)	-10(4)	-6(4)
C(2)	46(7)	29(5)	42(6)	9(5)	-14(6)	-8(5)
C(3)	27(5)	51(7)	38(5)	6(6)	-3(4)	-4(6)
C(4)	22(5)	23(4)	20(4)	-2(4)	2(4)	-1(4)
C(5)	41(6)	27(5)	23(5)	-1(4)	-5(5)	2(5)
C(6)	34(6)	26(5)	52(6)	2(5)	3(5)	4(5)
C(7)	18(5)	18(4)	30(5)	5(4)	3(4)	4(4)
C(8)	36(6)	24(5)	31(5)	-2(4)	9(5)	2(5)
C(9)	27(5)	33(5)	31(5)	-6(4)	-10(4)	2(5)
C(10)	11(4)	31(5)	37(5)	6(4)	-2(4)	4(4)
C(11)	42(8)	66(9)	57(8)	13(7)	3(7)	-9(7)
C(12)	20(5)	45(7)	50(6)	-1(5)	-2(5)	1(5)
F(1)	66(5)	26(3)	82(5)	31(3)	-29(4)	-17(3)
F(2)	76(5)	37(4)	89(5)	7(4)	-3(5)	23(4)
F(3)	65(5)	59(4)	50(4)	25(3)	-34(4)	0(4)
F(4)	21(3)	93(5)	55(4)	1(4)	11(3)	-13(4)
F(5)	53(4)	89(5)	31(3)	-10(4)	2(3)	-14(5)
F(6)	49(4)	52(4)	79(5)	-2(4)	0(4)	22(4)
F(7)	22(3)	57(4)	61(4)	3(3)	-1(3)	-2(3)
F(8)	46(4)	35(3)	44(3)	-1(3)	-4(3)	11(3)
F(9)	71(5)	74(5)	21(3)	-7(3)	-17(3)	11(4)
F(10)	56(4)	25(3)	46(3)	5(3)	6(3)	-10(3)
F(11)	41(4)	33(4)	118(6)	-1(4)	2(4)	17(3)
F(12)	86(5)	38(3)	38(3)	-17(3)	24(4)	-11(4)
F(13)	40(4)	44(3)	30(3)	7(3)	-2(3)	13(3)
F(14)	50(4)	35(3)	31(3)	-7(3)	8(3)	10(3)
F(15)	60(4)	34(3)	40(3)	8(3)	18(3)	-10(3)
F(16)	42(4)	32(3)	39(3)	-6(3)	7(3)	9(3)
F(17)	60(4)	26(3)	58(4)	-10(3)	9(3)	-17(3)
F(18)	65(5)	47(4)	28(3)	-1(3)	-13(3)	-2(4)
F(19)	96(7)	165(10)	53(5)	-22(6)	22(5)	-54(7)
F(20)	66(6)	113(7)	97(6)	0(5)	41(5)	38(5)
F(21)	73(6)	104(7)	69(5)	48(5)	21(5)	-14(5)
F(22)	47(5)	47(4)	102(6)	-3(4)	-8(4)	-19(4)
F(23)	28(4)	74(5)	102(6)	5(4)	-28(4)	12(4)
F(24)	42(4)	113(7)	51(4)	-20(5)	-1(3)	-18(5)

The anisotropic displacement factor exponent takes the form: $-2\pi^2((ha^*)^2U_{11} + \dots + 2hka^*b^*U_{12})$.

Table 17
Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{TlAl}(\text{OC}(\text{H})(\text{CF}_3)_2)_4$

	x	y	z	U(eq)
H(1A)	4783(7)	6278(9)	1039(5)	36(27)
H(4A)	5789(7)	6873(9)	4376(5)	49(32)
H(7A)	4523(6)	3744(8)	2888(5)	112(57)
H(10A)	3678(6)	7947(10)	2732(5)	71(40)

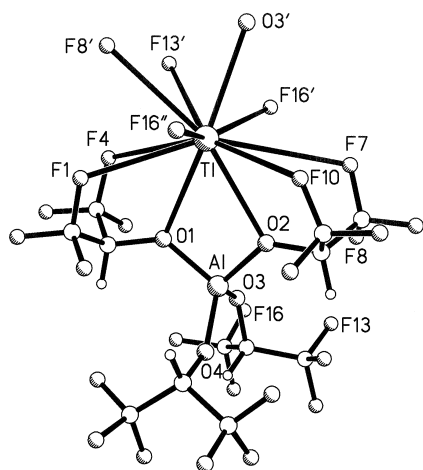


Fig. 5. Drawing of the structure of $\text{TlAl}(\text{OCH}(\text{CF}_3)_2)_4$. The unlabeled shaded circles are fluorine atoms, while the unlabeled open circles are carbon atoms (large) or hydrogen atoms (small). Selected interatomic distances (Å) and angles (deg): $\text{Tl}-\text{O}1$, 2.805(6); $\text{Tl}-\text{O}2$, 2.855(6); $\text{Tl}-\text{O}3'$, 2.992(6); $\text{Tl}-\text{F}1$, 3.090(7); $\text{Tl}-\text{F}4$, 3.398(7); $\text{Tl}-\text{F}7$, 3.540(6); $\text{Tl}-\text{F}10$, 2.967(6); other $\text{Tl}-\text{F}$, 3.045(6) to 3.245(6) Å; $\text{O}1-\text{Tl}-\text{O}2$, 54.3(2).

Table 18

Additional structural parameters for $\text{LiAl}(\text{HFPP})_4$, $\text{TlAl}(\text{HFTB})_4$, and $\text{TlAl}(\text{HFIP})_4$

	$\text{LiAl}(\text{HFPP})_4$	$\text{TlAl}(\text{HFTB})_4$	$\text{TlAl}(\text{HFIP})_4$
Distances (Å) ^b			
$\text{M} \cdots (\text{F}_4 \text{ plane})$	-0.70 ^c	0.37 ^d	0.75 ^d
$\text{O}1 \cdots (\text{F}_4 \text{ plane})$	-2.21	-1.99	-1.75
$\text{O}2 \cdots (\text{F}_4 \text{ plane})$	-2.21	-1.99	-1.76
$\text{F}1 \cdots (\text{F}_4 \text{ plane})$	0.13	-0.03	-0.05
$\text{F}4 \cdots (\text{F}_4 \text{ plane})$	-0.14	0.03	0.04
$\text{F}7 \cdots (\text{F}_4 \text{ plane})$	0.15	-0.03	-0.04
$\text{F}10 \cdots (\text{F}_4 \text{ plane})$	-0.14	0.03	0.05
Angles (deg)			
$\text{O}1-\text{M}-\text{O}2$	79.9(3) ^c	57.9(3) ^d	54.3(2) ^d
$\text{O}1-\text{Al}-\text{O}2$	91.8(1)	94.0(5)	95.8(3)
Dihedral of triangles ^e	12	111	85
MO_2F_4 bond-valence sum ^f			
	1.05	0.77	0.57

^a $\text{HFPP}^- = \text{OCH}(\text{CF}_3)_2^-$; $\text{HFTB}^- = \text{OC}(\text{CH}_3)(\text{CF}_3)_2^-$; $\text{HFIP}^- = \text{OCH}(\text{CF}_3)_2^-$.

^b The F_4 plane is the least-squares plane formed by F1, F4, F7 and F10.

^c $\text{M} = \text{Li}$.

^d $\text{M} = \text{Tl}$. ^e The dihedral angle of the least-squares planes formed by the $\text{O}1-\text{F}1-\text{F}4$ and $\text{O}2-\text{F}7-\text{F}10$ triangles.

^f The sum of metal-ligand bond valences for the six ligands O1, O2, F1, F4, F7 and F10.

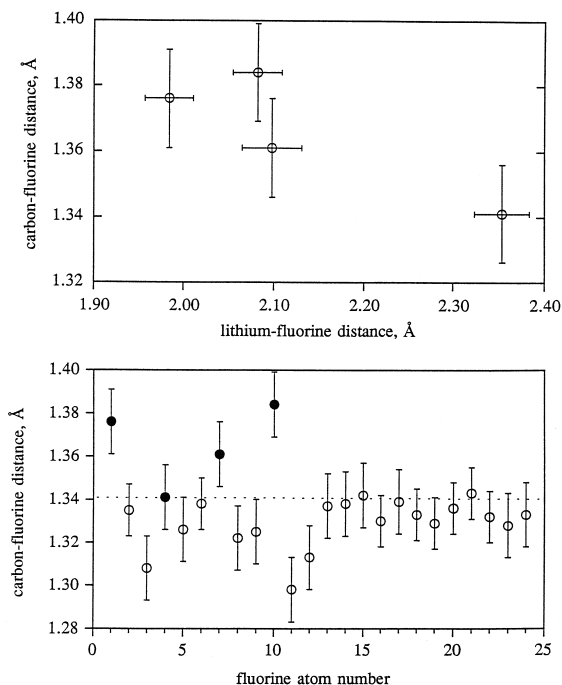


Fig. 6. Plots of C–F distance vs. Li–F distance and vs. fluorine atom number for $\text{LiAl}(\text{OC}(\text{Ph})(\text{CF}_3)_2)_4$. The error bars shown are ± 3 times the estimated standard deviation for each individual distance. The four points are at (1.984(9) Å, 1.376(5) Å), (2.082(9) Å, 1.384(5) Å), (2.098(11) Å, 1.361(5) Å), and (2.354(10) Å, 1.341(5) Å). In the bottom plot, the filled circles represent the four C–F(Li) bonds and the open circles represent the other twenty C–F bonds. The dotted line in the bottom plot is drawn through the C6–F4 distance of 1.341 Å.

$\text{LiAl}(\text{OC}(\text{CH}_3)(\text{CF}_3)_2)_4$ for 1,4 conjugate-addition reactions in toluene? The answer will depend, of course, on the mechanism. If dissociation of a Li–F(C) bond, which provides a coordination site for the carbonyl substrate, is rate limiting, then a greater number of intrinsically weaker Li–F(C) bonds would be preferred. If, however, attack of the nucleophile on the carbonyl carbon atom of the lithium-bound carbonyl substrate is rate limiting, then the Lewis acidity of the Li^+ catalyst minus one Li–F(C) bond is more important and fewer, stronger Li–F(C) bonds would be preferred.

The foregoing analysis is admittedly simplistic, both in the treatment of the factors discussed as well as in the exclusion of other factors. For example, the compound

Table 19

Bond–valences for $\text{LiAl}(\text{HFPP})_4$, $\text{TlAl}(\text{HFTB})_4$, and $\text{TlAl}(\text{HFIP})_4$ ^a

$\text{LiAl}(\text{HFPP})_4$			$\text{TlAl}(\text{HFTB})_4$			$\text{TlAl}(\text{HFIP})_4$		
bond	distance (Å)	bond valence	bond	distance (Å)	bond valence	bond	distance (Å)	bond valence
Li–O1	1.978(8)	0.230	Tl–O1	2.731(9)	0.207	Tl–O1	2.805(6)	0.176
Li–O2	1.966(8)	0.236	Tl–O2	2.717(9)	0.213	Tl–O2	2.855(6)	0.158
Li–F1	1.984(9)	0.185	Tl–F1	3.087(10)	0.072	Tl–F1	3.090(7)	0.072
Li–F4	2.354(10)	0.095	Tl–F4	2.903(9)	0.105	Tl–F4	3.398(7)	0.041
Li–F7	2.098(11)	0.149	Tl–F7	2.952(10)	0.095	Tl–F7	3.540(6)	0.032
Li–F10	2.082(9)	0.154	Tl–F10	3.081(11)	0.073	Tl–F10	2.967(6)	0.092
			Tl–F2'	3.339(10)	0.045	Tl–O3'	2.992(6)	0.120
Total bond valence =		1.049	Tl–F11'	3.240(10)	0.054	Tl–F8'	3.153(6)	0.064
			Tl–F19'	3.154(10)	0.064	Tl–F13'	3.245(6)	0.054
			Tl–F19''	3.471(10)	0.036	Tl–F16'	3.045(6)	0.079
			Tl–F20''	3.341(12)	0.045	Tl–F16''	3.242(5)	0.054
			total bond valence =	1.009		total bond valence =	0.942	

^a $\text{HFPP}^- = \text{OC}(\text{Ph})(\text{CF}_3)_2^-$; $\text{HFTB}^- = \text{OC}(\text{CH}_3)(\text{CF}_3)_2^-$; $\text{HFIP}^- = \text{OCH}(\text{CF}_3)_2^-$. The bond valence, s , is given by $s = (r/r_0)^{-N}$, where $r_0(\text{Li–F}) = 1.288$, $N(\text{Li–F}) = 3.9$, $r_0(\text{Tl–F}) = 1.993$, and $N(\text{Tl–F}) = 6.0$.

$\text{LiAl}(\text{OC}(\text{CH}_3)_2(\text{CF}_3))_4$ might very well contain intermolecular Li–F(C) bonds to compensate for the smaller number of CF_3 groups, and this might make the compound less soluble or even

insoluble in toluene. The discussion above was written to focus attention on one of the parameters that should be considered in the design of the next generation of weakly coordinating anions.

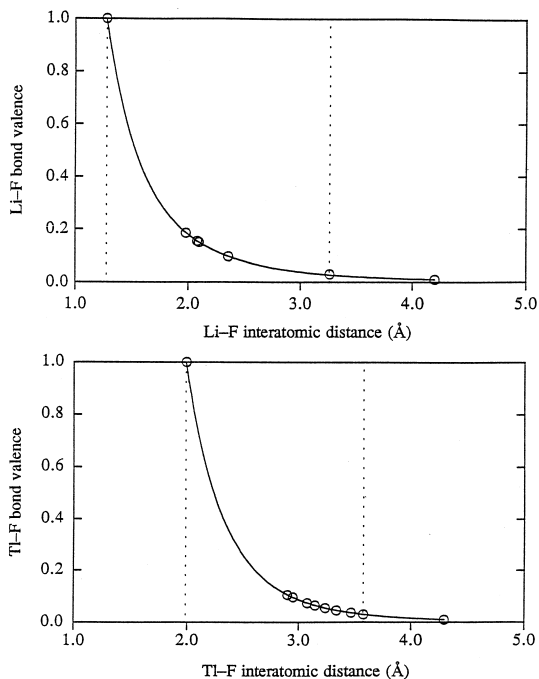


Fig. 7. Plots of M–F bond valence (s) vs. M–F distance for $\text{LiAl}(\text{OC}(\text{Ph})(\text{CF}_3)_2)_4$ ($M = \text{Li}$) and $\text{TlAl}(\text{OC}(\text{CH}_3)(\text{CF}_3)_2)_4$ ($M = \text{Tl}$). The dotted lines are drawn through M–F distances corresponding to $s = 1.0$ and $s = 0.03$. The right-most point in both plots corresponds to $s = 0.01$.

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