

Confinement of halide ions within homologous inverse hosts; modification of halide-ion selectivity

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ESI † Synthesis of the thf solvates **1Br**(Li2.5thf), **2Br**(Li5thf), **3Br**(Li2.5thf), **2I_{0.5}**(Li_{0.5}2.5thf) and **3I_{0.67}**(Li_{0.67}3.67thf)

All syntheses were carried out using strict inert-atmosphere techniques. The starting salts (EX₃) were acquired from Aldrich and were of the highest available purity.

PhPH₂ (0.33 mL, 3.0 mmol) was dissolved in thf (25 ml) and ⁿBuLi (3.75 mL, 6.0 mmol, 1.6 mol dm⁻³ in hexanes) was slowly added at room temperature. The yellow-green suspension was brought to reflux (4 h) and then added at room temperature to a solution of MeEX₂ in thf, prepared *in situ* by dropwise addition of MeLi (0.65 ml, 1.0 mmol, 1.0 mol dm⁻³ in Et₂O) at -78°C to a solution of EX₃ [1.0 mmol, X= Br, E= Al (0.27g), Ga (0.31g), In (0.35g); X= I, E= Ga (0.45g), In (0.49g)] dissolved in thf (10 ml). The stirred reaction mixture was allowed to warm to room temperature (45 min) and then brought to reflux overnight. The solvent was removed *in vacuo*, replaced by ether (20 ml) and filtered (P3, Celite) in order to separate the product from the insoluble LiX formed. After removing the ether from the filtrate *in vacuo*, the remaining yellow solid was dissolved in thf [4.0ml for **1Br**(Li2.5thf) and **3I_{0.67}**(Li_{0.67}3.67thf); 5.0ml for **2Br**(Li5thf) and **3Br**(Li2.5thf), **2I_{0.5}**(Li_{0.5}2.5thf)]. Storage at 5°C (7 days) gave high-quality cubic crystals of **1Br**(Li2.5thf) and **2Br**(Li5thf), while cubic crystals of **3Br**(Li2.5thf), **2I_{0.5}**(Li_{0.5}2.5thf) and **3I_{0.67}**(Li_{0.67}3.67thf) were obtained by storage at room temperature (24h).

Data for **1Br**; Yield 154 mg, 23% [on the basis of the crysta; formula **1Br**(Li2.5thf)], ¹H NMR (+ 25°C, 500.20 MHz, D₆-benzene), δ/ppm = 8.52-7.07 (m, C-H Ph), 3.52 (m, -CH₂-O thf), 1.35 (m, -CH₂- thf), 0.29 (s, Me-Al), ³¹P NMR (+ 25°C, 161.62MHz, thf with D₆-acetone capillary, rel. to 85% H₃PO₄/D₂O), δ/ppm= -159.7 (br.s.). ⁷Li NMR (+25°C, 194.40MHz, thf with D₆-acetone capillary, rel. to saturated LiCl/D₂O), δ/ppm = 1.85 (s) [br. shoulder at *ca.* 2.18], -0.32 (s). Elemental analysis C 58.2, H 7.7, P 10.9; calc. for **1Br**(Li2.5thf), C 59.6, H 7.0, P 13.7. Data for **2Br**(Li5thf); Yield 181 mg, 23%, [on the basis of **2Br**(Li5thf)]. ¹H NMR (+ 25 °C, 500.20 MHz, D₆-benzene), δ/ppm = 8.43 - 6.81 (m, C-H Ph), 3.50 (m, -CH₂-O thf), 1.30 (m, -CH₂- thf), 0.26 (s, Me-Ga), ³¹P NMR (+25 °C, 161.9MHz, thf with D₆-acetone capillary, rel. to 85% H₃PO₄/D₂O), δ/ppm = -148.9 (br. mult.). ⁷Li NMR (+25°C, 194.40 MHz, D₆-benzene, rel. to saturated LiCl/D₂O), δ/ppm = 2.64 (br. s), 1.80 (s). Elemental analysis C 55.4, H 7.6, P 10.3; calc. for **2Br**(Li5thf) C 56.8, H 7.0,

P 12.2. Data for **3Br**(Li2.5thf); Yield 175 mg, 23 %, ¹H NMR (+ 25 °C, 500.20 MHz, D₆-benzene), δ/ppm = 7.31-6.89 (m, C-H Ph), 3.41 (m, -CH₂-O thf), 1.24 (m, -CH₂- thf), 0.30 (s, Me-In). ³¹P NMR (+ 25 °C, 161.97MHz, thf with D₆-acetone capillary, rel. to 85% H₃PO₄/D₂O), δ/ppm = -164.0 (br.s.). ⁷Li NMR (+25°C, 194.40 MHz, D₆-benzene, rel. to saturated LiCl/D₂O), δ/ppm = 3.1 [br. shoulder at *ca.* δ1.7]. Elemental analysis C 51.1, H 6.0, P 10.8; calc. for **3Br**(Li2.5thf), C 52.7, H 6.2, P 12.2. Data for **2I_{0.5}**(Li_{0.5}2.5thf); Yield 78mg, 11 %. ¹H NMR (+ 25 °C, 500.20 MHz, D₆-benzene), δ/ppm = 7.24-6.40 (mult., C-H Ph), 3.59 (mult., -CH₂-O thf), 1.74 (mult., -CH₂- thf), 0.43 (s, Me-Ga). ³¹P NMR (202 MHz, 25°C, thf with D₆-acetone capillary) δ/ppm = -150.6 (mult.). Elemental analysis C 51.6, H 6.9, P 13.4; calc. for **2I_{0.5}**(Li_{0.5}2.5thf), C 57.8, H 6.8, P 13.4. Data for **3I_{0.67}**(Li_{0.67}3.67thf); Yield 73 mg, 9 % [on the basis of **3I_{0.67}**(Li_{0.67}3.67thf)], ¹H NMR (+ 25 °C, 500.20 MHz, D₆-benzene) δ/ppm = 8.23-6.80 (m, C-H Ph), 3.39 (m, -CH₂-O thf), 1.23 (m, -CH₂- thf), 0.29 (s, Me-In). ³¹P NMR (+25°C, 161.97 MHz, thf with D₆-acetone capillary, rel. to 85% H₃PO₄/D₂O), δ/ppm = -171.1 (br.mult.). ⁷Li NMR (+25 °C, 194.40 MHz, D₆-benzene, rel. to saturated LiCl/D₂O), δ/ppm = 3.0 (s) [br. shoulder at *ca.* δ1.5]. Elemental analysis C 50.0, H 6.5, P 9.4; calc. for **3I_{0.67}**(Li_{0.67}3.67thf), C 54.6, H 6.4, P 12.2.

[Comment- the elemental analysis was complicated by the loss of thf solvent from samples when exposed to a vacuum prior to isolation. The values quoted are typical of those obtained for each compound].

ESI ‡ X-ray Crystallography

Crystal data for Li_{1/2}[**1Br**]._{1/2}[Li(thf)₃].thf, [2Br][Li(thf)₄].thf, Li_{1/2}[**3Br**]._{1/2}[Li(thf)₄]._{1/2}thf, [2I_{0.5}]._{1/2}[Li(thf)₄]._{1/2}thf and [3I_{0.67}]._{3/5}[Li(thf)₄].thf; data were collected on a Nonius KappaCCD diffractometer at 180(2)K. The structures were solved by direct methods and in each case the heavy metal component of a 10-20% disorder with the enantiomer was located and included in full-matrix least squares refinement as a chiral twin on *F*² (G. M. Sheldrick, SHELX-97, Göttingen, Germany, 1997). See ESI ‡ for full details of the structural results.

Li_{1/2}[**1Br**]._{1/2}[Li(thf)₃].thf: C₁₃₄H₁₈₈Al₄BrLi₁₇O_{14.50}P₁₂, *M* = 2708.3, cubic, space group *F*-43c, *Z* = 8, *a* = 35.204(4)Å, *V* = 43282(9)Å³, μ(Mo-Kα) = 0.330mm⁻¹, ρ_{calc} = 0.825 Mg m⁻³. Total reflections collected 11370, unique 1848 (*R*int = 0.037). *R*1 = 0.066 [*I*>2σ(*I*)] and *wR*2 = 0.188 (all data).

[2Br][Li(thf)₄].thf: C₁₄₄H₁₉₆BrGa₄Li₁₇O₁₇P₁₂, *M* = 3047.42, cubic, space group *F*-43c, *Z* = 8, *a* = 35.133(4)Å, *V* = 43365(9)Å³, μ(Mo-Kα) = 0.806mm⁻¹, ρ_{calc} = 0.934 Mg m⁻³. Total reflections collected 20149, unique 3158 (*R*int = 0.043). *R*1 = 0.067 [*I*>2σ(*I*)] and *wR*2 = 0.223 (all data).

Li_{1/2}[**3Br**]._{1/2}[Li(thf)₄]._{1/2}thf: C₁₃₄H₁₈₈BrIn₄Li₁₇O_{14.50}P₁₂, *M* = 3059.65, cubic, space group *F*-43c, *Z* = 8, *a* = 35.110(4)Å, *V* = 43282(9)Å³, μ(Mo-Kα) = 0.732mm⁻¹, ρ_{calc} = 0.939Mg m⁻³. Total reflections collected 13481, unique 1854 (*R*int = 0.060). *R*1 = 0.070 [*I*>2σ(*I*)] and *wR*2 = 0.208 (all data).

[2I_{0.5}]._{1/2}[Li(thf)₄]._{1/2}thf: C₁₃₄H₁₈₈Ga₄I_{0.50}O_{14.50}P₁₂, *M* = 2859.32, cubic, space group *F*-43c, *Z* = 8, *a* = 35.019(4)Å, *V* = 42944(8)Å³, μ(Mo-Kα) = 0.696mm⁻¹, ρ_{calc} = 0.885 Mg m⁻³. Total reflections collected 31422, unique 1888 (*R*int = 0.045). *R*1 = 0.052 [*I*>2σ(*I*)] and *wR*2 = 0.151 (all data).

[3I_{0.67}]._{3/5}[Li(thf)₄].thf: C_{138.67}H_{193.33}I_{0.67}In₄Li_{16.67}O_{15.67}P₁₂, *M* = 3142.12, cubic, space group *F*-43c, *Z* = 8, *a* = 35.312(4)Å, *V* = 44033(9)Å³, μ(Mo-Kα) = 0.633mm⁻¹, ρ_{calc} = 0.948 Mg m⁻³. Total reflections collected 7636, unique 1592 (*R*int = 0.048). *R*1 = 0.070 [*I*>2σ(*I*)] and *wR*2 = 0.212x (all data).

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115 Data for $\text{Li}_2[\mathbf{1Br}] \cdot \frac{1}{2}[\text{Li}(\text{thf})_3] \cdot \text{thf}$, $[\mathbf{2Br}][\text{Li}(\text{thf})_4] \cdot \text{thf}$,
 $\text{Li}_2[\mathbf{3Br}] \cdot \frac{1}{2}[\text{Li}(\text{thf})_4] \cdot \frac{1}{2}\text{thf}$, $[\mathbf{2I}_{0.5}] \cdot \frac{1}{2}[\text{Li}(\text{thf})_4] \cdot \frac{1}{2}\text{thf}$ and $[\mathbf{3I}_{0.67}] \cdot \frac{2}{3}[\text{Li}(\text{thf})_4] \cdot \text{thf}$
can be obtained free of charge via
www.ccdc.cam.ac.uk/conts/retrieving.html (or from The Cambridge
Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK;
120 fax: +44 1223 336 033; deposit@ccdc.cam.ac.uk).

Data were collected on a Nonius KappaCCD diffractometer at
180(2)K. The structures were solved by direct methods and the
atoms of the giant cluster anions were located readily with the
125 central halide anion located on a site of 23 symmetry so the
asymmetric unit in each consists of single PPh, EMe, Li(thf) and
LiX group. In each case there was an isolated residual maximum
centrosymmetrically related to the heavy metal (E1). This was
attributed to small disorder of the cluster cage with its enantiomer.

130 Only the heavy metal component of the minor disorder component
was included in the refinement [occupancies ca. 7 % Al in
 $\mathbf{1Br}(\text{Li}2.5\text{thf})$, and 10 and 13 % Ga in $\mathbf{2Br}(\text{Li}5\text{thf})$ and
 $\mathbf{2I}_{0.5}(\text{Li}_{0.5}2.5\text{thf})$, respectively, and 18 % In in $\mathbf{3Br}(\text{Li}2.5\text{thf})$ and
 $\mathbf{3I}_{0.67}(\text{Li}_{0.67}3.67\text{thf})$, respectively. In each cluster anion there was a
135 conformational disorder of 2 C-atoms of the thf group of the the
unique Li(thf) ligand of the cluster. In $\mathbf{2I}_{0.5}(\text{Li}_{0.5}2.5\text{thf})$ and
 $\mathbf{3I}_{0.67}(\text{Li}_{0.67}3.67\text{thf})$ reasonable displacement parameters for the
iodide atom at the centre of each cluster was achieved by assigning
it partial occupancy (0.50 in $\mathbf{2I}_{0.5}(\text{Li}_{0.5}2.5\text{thf})$ and 0.67 in
140 $\mathbf{3I}_{0.67}(\text{Li}_{0.67}3.67\text{thf})$).

Only in the structures of $\mathbf{3Br}(\text{Li}2.5\text{thf})$ and $\mathbf{2I}_{0.5}(\text{Li}_{0.5}2.5\text{thf})$ were
complete $[\text{Li}(\text{thf})_4]^+$ counter anions unambiguously identified, and
in each the Li^+ cation lies on a 3-fold axis relating three of the THF
ligands and the fourth thf is severely disordered across a site of 23
145 symmetry. In each of $\mathbf{2Br}(\text{Li}5\text{thf})$ and $\mathbf{3I}_{0.67}(\text{Li}_{0.67}3.67\text{thf})$ a
poorly defined thf group (thought initially to be a solvate molecule)
was shown to belong to a $[\text{Li}(\text{thf})_4]^+$ cation by introducing an Li
atom at the site identified in $\mathbf{3Br}(\text{Li}2.5\text{thf})$ and $\mathbf{2I}_{0.5}(\text{Li}_{0.5}2.5\text{thf})$.
In each of the structures $\mathbf{2Br}(\text{Li}5\text{thf})$ and $\mathbf{3I}_{0.67}(\text{Li}_{0.67}3.67\text{thf})$
150 residual maxima of electron across a site of 23 symmetry was
assigned as the atoms of the highly disordered fourth thf and were
included in the refinement without their H-atoms. In $\mathbf{1Br}$ a unique
thf group near a 3-fold axis was identified as part of a $\text{Li}(\text{thf})^{3+}$
cation but all attempts to locate a possible fourth THF were
155 unsuccessful. Constraints were applied to idealise the geometry of
the fully identified THF group of each cations. An isolated group of
2 or 3 residual maxima on site of -4 symmetry at $\frac{3}{4}$, $\frac{3}{4}$, $\frac{1}{2}$ were
assigned arbitrarly as partial C- or O- atoms to correspond to one
thf solvate per cluster in the crystals of $\mathbf{1Br}(\text{Li}2.5\text{thf})$, $\mathbf{2Br}$ and $\mathbf{3I}$,
160 and a half thf solvate in $\mathbf{3Br}(\text{Li}2.5\text{thf})$ and $\mathbf{2I}_{0.5}(\text{Li}_{0.5}2.5\text{thf})$; they
were included in the refinement without any contribution from their
H-atoms.

Anisotropic displacement parameters were applied to full
occupancy atoms in all structures, which were treated as chiral
165 twins in the in full-matrix least squares refinement on F^2 (G. M.
Sheldrick, SHELX-97, Göttingen, Germany, 1997).