

# Crystal structure of dimethyl-1 $\kappa^2$ C-bis( $\mu$ -4-methylphenolato-1:2 $\kappa^2$ O:O)( $N,N,N',N'$ -tetramethylethylenediamine-2 $\kappa^2$ $N,N'$ )-indium(III)lithium(I)

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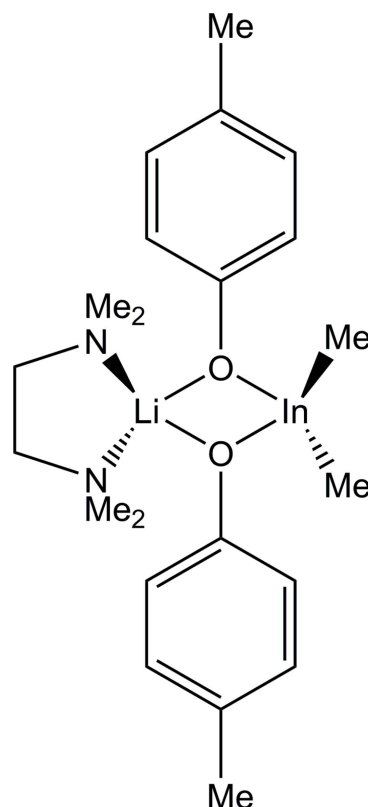
The mixed bimetallic title compound, [InLi(CH<sub>3</sub>)<sub>2</sub>(C<sub>7</sub>H<sub>7</sub>O)<sub>2</sub>(C<sub>6</sub>H<sub>16</sub>N<sub>2</sub>)] or [(tmeda)Li- $\mu$ -(4-MeC<sub>6</sub>H<sub>4</sub>O)<sub>2</sub>InMe<sub>2</sub>] (tmeda is  $N,N,N',N'$ -tetramethylethylenediamine), exhibits a four-membered LiO<sub>2</sub>In ring core *via* bridging 4-methylphenolate groups. The Li and In atoms are in distorted tetrahedral N<sub>2</sub>O<sub>2</sub> and C<sub>2</sub>O<sub>2</sub> bonding environments, respectively. The Li atom is further chelated by a tmeda group, yielding a spirocyclic structure.

**Keywords:** crystal structure; bimetallic; indium; lithium; phenolate; spirocyclic.

**CCDC reference:** 1440726

## 1. Related literature

For other bimetallic alkali–triel chalcogenolates, see: Niemeyer & Power (1997); Clegg *et al.* (1999); Muñoz *et al.* (2011, 2014); Uhl *et al.* (1994); Adonin *et al.* (2005); Soki *et al.* (2008); Normand *et al.* (2012). For metal-containing ligands, see Simmonds & Wright (2012). For organometallic precursors for indium tin oxide (ITO), see: Aksu & Driess (2009); Veith & Kunze (1991). For dimeric dimethylindium phenolates [Me<sub>2</sub>InOR]<sub>2</sub>, see: Briand *et al.* (2013, 2010); Beachley *et al.* (2003); Häusslein *et al.* (1999); Blake *et al.* (2011); Bradley *et al.* (1988); Trentler *et al.* (1997).



## 2. Experimental

### 2.1. Crystal data

[InLi(CH<sub>3</sub>)<sub>2</sub>(C<sub>7</sub>H<sub>7</sub>O)<sub>2</sub>(C<sub>6</sub>H<sub>16</sub>N<sub>2</sub>)]  
 $M_r = 482.29$   
 Monoclinic,  $P2_1/c$   
 $a = 9.0991$  (8) Å  
 $b = 16.4481$  (15) Å  
 $c = 16.4256$  (15) Å  
 $\beta = 91.956$  (1)°

$V = 2456.9$  (4) Å<sup>3</sup>  
 $Z = 4$   
 Mo  $K\alpha$  radiation  
 $\mu = 0.98$  mm<sup>-1</sup>  
 $T = 188$  K  
 $0.65 \times 0.60 \times 0.60$  mm

### 2.2. Data collection

Bruker SMART1000/P4  
 diffractometer  
 Absorption correction: multi-scan  
 (SADABS; Sheldrick, 2008a)  
 $T_{\min} = 0.569$ ,  $T_{\max} = 0.591$

16648 measured reflections  
 5459 independent reflections  
 4921 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.025$

### 2.3. Refinement

$R[F^2 > 2\sigma(F^2)] = 0.025$   
 $wR(F^2) = 0.067$   
 $S = 1.05$   
 5459 reflections

261 parameters  
 H-atom parameters constrained  
 $\Delta\rho_{\text{max}} = 0.56$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.27$  e Å<sup>-3</sup>

Data collection: SMART (Bruker, 1999); cell refinement: SAINT (Bruker, 2006); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008b); program(s) used to refine structure: SHELXL2013 (Sheldrick, 2015); molecular graphics: DIAMOND (Brandenburg, 2012); software used to prepare material for publication: SHELXTL (Sheldrick, 2008b).

## Acknowledgements

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Supporting information for this paper is available from the IUCr electronic archives (Reference: LH5799).

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## supporting information

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## Crystal structure of dimethyl-1 $\kappa^2$ C-bis( $\mu$ -4-methylphenolato-1:2 $\kappa^2$ O:O) (*N,N,N',N'*-tetramethylethylenediamine-2 $\kappa^2$ N,N')indium(III)lithium(I)

Glen G. Briand, Andreas Decken and Marshall R. Hoey

### S1. Comment

Ligands containing metal bridgeheads are useful for the generation of mixed metal species with novel physical properties and reactivity (Simmonds *et al.*, 2012). In our efforts to generate organometallic In/Sn precursors for indium tin oxide (ITO) semiconductor species (Aksu *et al.*, 2009; Veith *et al.*, 1991), we have isolated the Li<sup>+</sup> salt of the anionic ligand [(4-MeC<sub>6</sub>H<sub>4</sub>O)<sub>2</sub>InMe<sub>2</sub>]<sup>-</sup>. The structure of [(tmeda)Li- $\mu$ -(4-MeC<sub>6</sub>H<sub>4</sub>O)<sub>2</sub>InMe<sub>2</sub>] (tmeda = *N,N,N',N'*-tetramethylethylenediamine) (**I**) (Fig. 1) exhibits a four-membered LiO<sub>2</sub>In ring core in which Li1 and In1 centre are bridged *via* the oxygen atoms of two 4-MeC<sub>6</sub>H<sub>4</sub>O ligands. The In—O bond distances [In1—O1 = 2.125 (1), In1—O2 = 2.141 (1) Å] are larger than the Li—O bond distances [Li1—O1 = 1.889 (4), Li1—O2 = 1.926 (3) Å] as a result of the larger covalent radius of In *versus* Li. However, the LiO<sub>2</sub>In ring is nearly planar [In1—O1—Li1—O2 = -4.5 (1)°]. In addition to the In—O bonds, In1 is also bonded to the carbon atoms of two methyl groups, resulting in a distorted tetrahedral C<sub>2</sub>O<sub>2</sub> bonding environment for indium [O1—In1—O2 = 78.32 (5), C1—In1—C2 = 133.8 (1)°]. Li1 is also bonded to two nitrogen atoms of a chelating tmeda ligand, resulting in a distorted tetrahedral N<sub>2</sub>O<sub>2</sub> bonding environment for lithium [O1—Li1—O2 = 89.9 (2), N1—In1—N2 = 86.8 (2)°]. The overall result is a bimetallic spirocyclic arrangement. The 4-MeC<sub>6</sub>H<sub>5</sub> rings are displaced slightly toward the Me<sub>2</sub>In group [C3—O1—In1 = 121.0 (1), C10—O2—In1 = 125.0 (1), C3—O1—Li1 = 142.4 (2), C10—O2—Li1 = 137.9 (2)°] and are nearly orthogonal [88.63 (6)°]. The geometries at the bridging O atoms are distorted trigonal planar [ $\Sigma$  X—O1—X = 360.0,  $\Sigma$  X—O2—X = 357.9°]. The structure resembles those of dimethylindium phenolates [Me<sub>2</sub>InOR]<sub>2</sub>, which form bimetallic species in the solid state *via* intermolecular In—O coordinate bonding interactions (Briand *et al.*, 2013; Briand *et al.*, 2010; Beachley *et al.*, 2003; Häußlein *et al.*, 1999; Blake *et al.*, 2011; Bradley *et al.*, 1988; Trentler *et al.*, 1997). These structures feature distorted tetrahedral geometries at In, distorted trigonal planar or slightly pyramidal geometries at O, and near planar In<sub>2</sub>O<sub>2</sub> ring cores. For other bimetallic alkali-triethyl chalcogenolates, see: Niemeyer *et al.* (1997); Clegg *et al.* (1999); Muñoz *et al.* (2011); Uhl *et al.* (1994); Adonin *et al.* (2005); Soki *et al.* (2008); Muñoz *et al.* (2014); Normand *et al.* (2012).

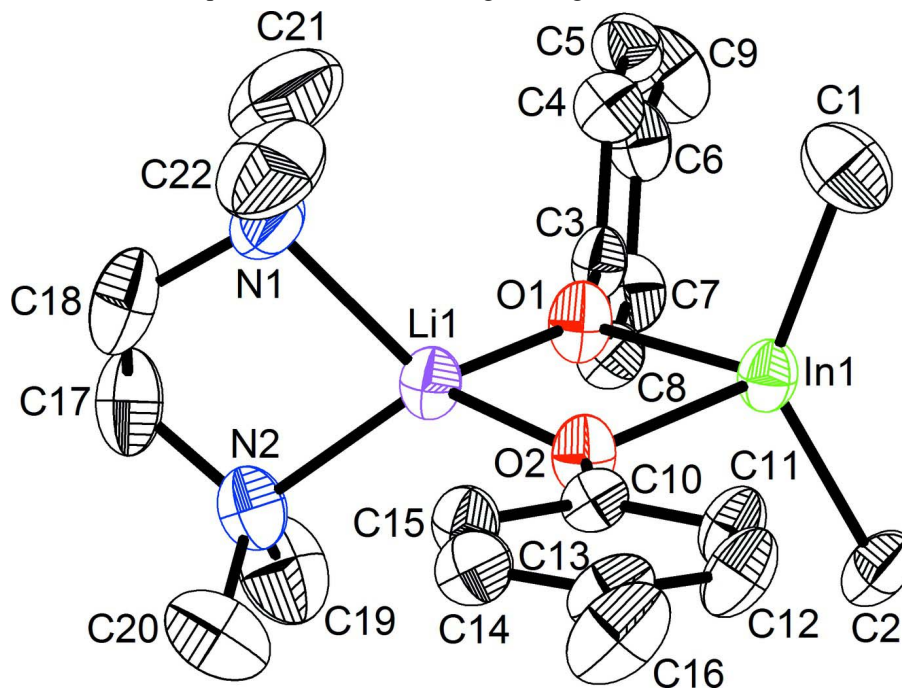
### S2. Synthesis and Crystallization

Synthesis of [(tmeda)Li- $\mu$ -(4-MeC<sub>6</sub>H<sub>4</sub>O)<sub>2</sub>InMe<sub>2</sub>]. [4-MeC<sub>6</sub>H<sub>4</sub>O]Li (0.143 g, 1.25 mmol) was added to a stirred solution of InMe<sub>3</sub> (0.200 g, 1.25 mmol) in diethyl ether (10 ml). After 1 h, 4-MeC<sub>6</sub>H<sub>4</sub>OH (0.064 g, 0.60 mmol) in diethyl ether (3 ml) was added. After 2 h, tmeda (0.145 g, 1.25 mmol) was added. After 1 h, the reaction mixture was filtered, and the filtrate concentrated to 5 ml and allowed to sit at 277 K. After 1 d, the solution was filtered to yield colourless crystals of **I** (0.188 g, 0.490 mmol, 82%). Anal. Calc. for C<sub>22</sub>H<sub>36</sub>InLiN<sub>2</sub>O<sub>2</sub>: C, 54.78; H, 7.52; N, 5.81. Found: C, 54.56; H, 8.01; N, 5.67. Mp 426–428 K. FT-Raman (cm<sup>-1</sup>): 127 s, 170 m, 297 w, 342 w, 502 vs [*v*<sub>sym</sub> (Me—In—Me)], 519 w [*v*<sub>asym</sub> (Me—In—Me)], 646 w, 766 m, 791 m, 857 m, 1155 m, 1212 w, 1288 w, 1383 w, 1438 w, 1607 w, 2841 w, 2921 m, 2959 m, 3045 w. <sup>1</sup>H NMR (thf-*d*<sub>8</sub>, p.p.m.): 0.00 (s, 6H, Me<sub>2</sub>In), 2.31 (s, 6H, MeC<sub>6</sub>H<sub>4</sub>), 2.33 (s, 12H, Me<sub>2</sub>N), 2.48 (s, 4H, NCH<sub>2</sub>), 6.60 (d,

$^3J_{\text{H-H}} = 11$  Hz, 4H,  $\text{C}_6\text{H}_4$ ), 6.96 (d,  $^3J_{\text{H-H}} = 11$  Hz, 4H,  $\text{C}_6\text{H}_4$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (thf- $d_8$ , p.p.m.): -1.8 ( $\text{Me}_2\text{In}$ ), 19.8 ( $\text{MeC}_6\text{H}_4$ ), 45.4 ( $\text{Me}_2\text{N}$ ), 58.2 (NCH<sub>2</sub>), 118.0 ( $\text{C}_6\text{H}_4$ ), 129.5 ( $\text{C}_6\text{H}_4$ ).

### S3. Refinement

H atoms were included in calculated positions and refined using a riding model.



**Figure 1**

The molecular structure of (**I**), with displacement ellipsoids drawn at the 50% probability level. H atoms have been omitted for clarity.

### Dimethyl-1,2-ethanedithiolate-1:2- $\kappa^2$ O:O)(*N,N,N',N'*-tetramethylethylenediamine-2- $\kappa^2$ N,N')indium(III)lithium(I)

#### Crystal data

$[\text{InLi}(\text{CH}_3)_2(\text{C}_7\text{H}_7\text{O})_2(\text{C}_6\text{H}_{16}\text{N}_2)]$

$M_r = 482.29$

Monoclinic,  $P2_1/c$

$a = 9.0991$  (8) Å

$b = 16.4481$  (15) Å

$c = 16.4256$  (15) Å

$\beta = 91.956$  (1)°

$V = 2456.9$  (4) Å<sup>3</sup>

$Z = 4$

$F(000) = 1000$

$D_x = 1.304$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 5977 reflections

$\theta = 2.5$ – $28.4$ °

$\mu = 0.98$  mm<sup>-1</sup>

$T = 188$  K

Irregular, colourless

$0.65 \times 0.60 \times 0.60$  mm

#### Data collection

Bruker SMART1000/P4  
diffractometer

Radiation source: fine-focus sealed tube, K760

Graphite monochromator

$\varphi$  and  $\omega$  scans

Absorption correction: multi-scan  
(*SADABS*; Sheldrick, 2008a)

$T_{\text{min}} = 0.569$ ,  $T_{\text{max}} = 0.591$

16648 measured reflections

5459 independent reflections

4921 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.025$   
 $\theta_{\text{max}} = 27.5^\circ$ ,  $\theta_{\text{min}} = 1.8^\circ$   
 $h = -11 \rightarrow 11$

$k = -21 \rightarrow 21$   
 $l = -21 \rightarrow 20$

### Refinement

Refinement on  $F^2$   
 Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.025$   
 $wR(F^2) = 0.067$   
 $S = 1.05$   
 5459 reflections  
 261 parameters  
 0 restraints  
 Primary atom site location: structure-invariant  
 direct methods

Secondary atom site location: difference Fourier  
 map  
 Hydrogen site location: inferred from  
 neighbouring sites  
 H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.0318P)^2 + 1.1193P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.002$   
 $\Delta\rho_{\text{max}} = 0.56 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.26 \text{ e } \text{\AA}^{-3}$

### Special details

**Experimental.** Crystal decay was monitored by repeating the initial 50 frames at the end of the data collection and analyzing duplicate reflections

**Geometry.** All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

### Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

|     | <i>x</i>     | <i>y</i>      | <i>z</i>     | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|--------------|---------------|--------------|----------------------------------|
| In1 | 0.26596 (2)  | 0.05874 (2)   | 0.78772 (2)  | 0.03548 (6)                      |
| O1  | 0.37283 (15) | 0.14787 (8)   | 0.71713 (8)  | 0.0396 (3)                       |
| O2  | 0.12094 (14) | 0.16051 (8)   | 0.79780 (8)  | 0.0390 (3)                       |
| Li1 | 0.2425 (4)   | 0.2341 (2)    | 0.7385 (2)   | 0.0375 (7)                       |
| N1  | 0.3343 (2)   | 0.34149 (12)  | 0.79061 (12) | 0.0511 (5)                       |
| N2  | 0.1764 (2)   | 0.30590 (12)  | 0.63874 (11) | 0.0489 (4)                       |
| C1  | 0.3935 (4)   | 0.04698 (19)  | 0.89888 (16) | 0.0686 (8)                       |
| H1A | 0.4979       | 0.0543        | 0.8879       | 0.103*                           |
| H1B | 0.3783       | -0.0072       | 0.9220       | 0.103*                           |
| H1C | 0.3628       | 0.0884        | 0.9376       | 0.103*                           |
| C2  | 0.1651 (2)   | -0.02775 (13) | 0.70346 (14) | 0.0475 (5)                       |
| H2A | 0.0581       | -0.0208       | 0.7024       | 0.071*                           |
| H2B | 0.1899       | -0.0831       | 0.7211       | 0.071*                           |
| H2C | 0.2016       | -0.0185       | 0.6488       | 0.071*                           |
| C3  | 0.4953 (2)   | 0.12953 (11)  | 0.67653 (11) | 0.0333 (4)                       |
| C4  | 0.6347 (2)   | 0.13756 (12)  | 0.71342 (11) | 0.0382 (4)                       |
| H4  | 0.6443       | 0.1558        | 0.7682       | 0.046*                           |
| C5  | 0.7597 (2)   | 0.11910 (13)  | 0.67083 (12) | 0.0408 (4)                       |
| H5  | 0.8537       | 0.1252        | 0.6971       | 0.049*                           |
| C6  | 0.7502 (2)   | 0.09210 (13)  | 0.59107 (12) | 0.0415 (4)                       |
| C7  | 0.6121 (2)   | 0.08379 (13)  | 0.55467 (12) | 0.0426 (5)                       |
| H7  | 0.6032       | 0.0653        | 0.4999       | 0.051*                           |
| C8  | 0.4854 (2)   | 0.10193 (12)  | 0.59630 (12) | 0.0384 (4)                       |

|      |             |              |              |             |
|------|-------------|--------------|--------------|-------------|
| H8   | 0.3917      | 0.0955       | 0.5699       | 0.046*      |
| C9   | 0.8866 (3)  | 0.06967 (18) | 0.54574 (16) | 0.0625 (7)  |
| H9A  | 0.9076      | 0.0117       | 0.5534       | 0.094*      |
| H9B  | 0.9702      | 0.1018       | 0.5669       | 0.094*      |
| H9C  | 0.8702      | 0.0810       | 0.4876       | 0.094*      |
| C10  | 0.0086 (2)  | 0.16495 (12) | 0.84883 (11) | 0.0334 (4)  |
| C11  | -0.0424 (2) | 0.09752 (13) | 0.89039 (13) | 0.0415 (4)  |
| H11  | 0.0019      | 0.0460       | 0.8824       | 0.050*      |
| C12  | -0.1578 (3) | 0.10467 (14) | 0.94352 (14) | 0.0502 (5)  |
| H12  | -0.1910     | 0.0575       | 0.9708       | 0.060*      |
| C13  | -0.2252 (2) | 0.17834 (15) | 0.95769 (13) | 0.0471 (5)  |
| C14  | -0.1765 (2) | 0.24514 (14) | 0.91485 (13) | 0.0458 (5)  |
| H14  | -0.2227     | 0.2963       | 0.9220       | 0.055*      |
| C15  | -0.0617 (2) | 0.23886 (13) | 0.86159 (12) | 0.0407 (4)  |
| H15  | -0.0305     | 0.2859       | 0.8333       | 0.049*      |
| C16  | -0.3460 (3) | 0.18714 (19) | 1.01892 (18) | 0.0705 (8)  |
| H16A | -0.4306     | 0.2151       | 0.9931       | 0.106*      |
| H16B | -0.3090     | 0.2188       | 1.0658       | 0.106*      |
| H16C | -0.3762     | 0.1331       | 1.0372       | 0.106*      |
| C17  | 0.2618 (4)  | 0.37967 (17) | 0.64916 (18) | 0.0716 (8)  |
| H17A | 0.2149      | 0.4236       | 0.6164       | 0.086*      |
| H17B | 0.3615      | 0.3706       | 0.6285       | 0.086*      |
| C18  | 0.2747 (4)  | 0.40580 (16) | 0.7358 (2)   | 0.0719 (8)  |
| H18A | 0.3396      | 0.4540       | 0.7399       | 0.086*      |
| H18B | 0.1764      | 0.4221       | 0.7540       | 0.086*      |
| C19  | 0.2068 (4)  | 0.2688 (2)   | 0.55914 (15) | 0.0742 (8)  |
| H19A | 0.1775      | 0.3065       | 0.5154       | 0.111*      |
| H19B | 0.1509      | 0.2181       | 0.5528       | 0.111*      |
| H19C | 0.3121      | 0.2571       | 0.5565       | 0.111*      |
| C20  | 0.0174 (3)  | 0.3218 (2)   | 0.64082 (18) | 0.0748 (8)  |
| H20A | -0.0056     | 0.3462       | 0.6933       | 0.112*      |
| H20B | -0.0365     | 0.2705       | 0.6339       | 0.112*      |
| H20C | -0.0115     | 0.3592       | 0.5967       | 0.112*      |
| C21  | 0.4918 (3)  | 0.3336 (2)   | 0.7846 (3)   | 0.1069 (14) |
| H21A | 0.5149      | 0.3171       | 0.7291       | 0.160*      |
| H21B | 0.5284      | 0.2924       | 0.8233       | 0.160*      |
| H21C | 0.5389      | 0.3859       | 0.7972       | 0.160*      |
| C22  | 0.2953 (4)  | 0.3605 (2)   | 0.87428 (18) | 0.0885 (10) |
| H22A | 0.3377      | 0.3194       | 0.9114       | 0.133*      |
| H22B | 0.1881      | 0.3606       | 0.8781       | 0.133*      |
| H22C | 0.3341      | 0.4142       | 0.8894       | 0.133*      |

Atomic displacement parameters ( $\text{\AA}^2$ )

|     | $U^{11}$    | $U^{22}$    | $U^{33}$    | $U^{12}$     | $U^{13}$    | $U^{23}$    |
|-----|-------------|-------------|-------------|--------------|-------------|-------------|
| In1 | 0.03663 (9) | 0.03030 (8) | 0.04007 (8) | -0.00028 (5) | 0.00951 (6) | 0.00208 (5) |
| O1  | 0.0382 (7)  | 0.0336 (7)  | 0.0480 (7)  | 0.0027 (6)   | 0.0178 (6)  | 0.0033 (6)  |
| O2  | 0.0386 (7)  | 0.0350 (7)  | 0.0443 (7)  | 0.0027 (6)   | 0.0159 (6)  | 0.0039 (6)  |

|     |             |             |             |              |              |              |
|-----|-------------|-------------|-------------|--------------|--------------|--------------|
| Li1 | 0.0400 (17) | 0.0319 (16) | 0.0410 (16) | -0.0002 (13) | 0.0065 (13)  | 0.0024 (13)  |
| N1  | 0.0498 (11) | 0.0399 (10) | 0.0635 (12) | -0.0054 (8)  | 0.0004 (9)   | -0.0099 (9)  |
| N2  | 0.0563 (11) | 0.0452 (10) | 0.0454 (9)  | 0.0051 (9)   | 0.0050 (8)   | 0.0086 (8)   |
| C1  | 0.0794 (19) | 0.079 (2)   | 0.0467 (13) | 0.0079 (15)  | -0.0064 (13) | 0.0139 (13)  |
| C2  | 0.0454 (12) | 0.0363 (11) | 0.0613 (13) | -0.0092 (9)  | 0.0056 (10)  | -0.0113 (10) |
| C3  | 0.0357 (9)  | 0.0257 (9)  | 0.0390 (9)  | 0.0004 (7)   | 0.0109 (7)   | 0.0026 (7)   |
| C4  | 0.0403 (10) | 0.0406 (10) | 0.0338 (9)  | 0.0028 (8)   | 0.0047 (8)   | -0.0026 (8)  |
| C5  | 0.0340 (10) | 0.0437 (11) | 0.0449 (10) | 0.0035 (8)   | 0.0025 (8)   | 0.0018 (9)   |
| C6  | 0.0427 (11) | 0.0387 (11) | 0.0441 (10) | 0.0097 (9)   | 0.0145 (9)   | 0.0038 (9)   |
| C7  | 0.0524 (12) | 0.0421 (11) | 0.0337 (9)  | 0.0043 (9)   | 0.0078 (8)   | -0.0047 (8)  |
| C8  | 0.0375 (10) | 0.0367 (10) | 0.0411 (9)  | -0.0021 (8)  | 0.0027 (8)   | -0.0021 (8)  |
| C9  | 0.0531 (14) | 0.0774 (18) | 0.0584 (14) | 0.0221 (13)  | 0.0217 (12)  | 0.0033 (13)  |
| C10 | 0.0319 (9)  | 0.0356 (10) | 0.0329 (8)  | -0.0025 (7)  | 0.0048 (7)   | -0.0049 (7)  |
| C11 | 0.0453 (11) | 0.0326 (10) | 0.0475 (10) | -0.0047 (8)  | 0.0158 (9)   | -0.0079 (9)  |
| C12 | 0.0567 (13) | 0.0429 (12) | 0.0525 (12) | -0.0154 (10) | 0.0244 (10)  | -0.0091 (10) |
| C13 | 0.0376 (10) | 0.0536 (13) | 0.0512 (11) | -0.0087 (9)  | 0.0145 (9)   | -0.0189 (10) |
| C14 | 0.0381 (10) | 0.0452 (12) | 0.0546 (12) | 0.0059 (9)   | 0.0073 (9)   | -0.0123 (10) |
| C15 | 0.0388 (10) | 0.0376 (10) | 0.0461 (10) | 0.0028 (8)   | 0.0073 (8)   | -0.0001 (9)  |
| C16 | 0.0580 (15) | 0.0729 (18) | 0.0832 (18) | -0.0151 (13) | 0.0398 (14)  | -0.0275 (15) |
| C17 | 0.093 (2)   | 0.0459 (14) | 0.0762 (18) | -0.0046 (14) | 0.0121 (16)  | 0.0229 (13)  |
| C18 | 0.092 (2)   | 0.0334 (12) | 0.091 (2)   | -0.0066 (13) | 0.0130 (17)  | -0.0044 (13) |
| C19 | 0.100 (2)   | 0.077 (2)   | 0.0470 (13) | 0.0161 (17)  | 0.0141 (14)  | 0.0074 (13)  |
| C20 | 0.0626 (16) | 0.100 (2)   | 0.0619 (15) | 0.0196 (16)  | -0.0017 (13) | 0.0061 (16)  |
| C21 | 0.0563 (18) | 0.080 (2)   | 0.184 (4)   | -0.0067 (16) | -0.005 (2)   | -0.043 (3)   |
| C22 | 0.117 (3)   | 0.085 (2)   | 0.0633 (17) | -0.023 (2)   | -0.0025 (17) | -0.0287 (17) |

*Geometric parameters (Å, °)*

|        |             |          |           |
|--------|-------------|----------|-----------|
| In1—O1 | 2.1252 (13) | C9—H9B   | 0.9800    |
| In1—C1 | 2.138 (3)   | C9—H9C   | 0.9800    |
| In1—O2 | 2.1414 (13) | C10—C11  | 1.391 (3) |
| In1—C2 | 2.167 (2)   | C10—C15  | 1.393 (3) |
| O1—C3  | 1.352 (2)   | C11—C12  | 1.393 (3) |
| O1—Li1 | 1.889 (4)   | C11—H11  | 0.9500    |
| O2—C10 | 1.346 (2)   | C12—C13  | 1.382 (3) |
| O2—Li1 | 1.926 (3)   | C12—H12  | 0.9500    |
| Li1—N2 | 2.092 (4)   | C13—C14  | 1.386 (3) |
| Li1—N1 | 2.122 (4)   | C13—C16  | 1.522 (3) |
| N1—C21 | 1.446 (4)   | C14—C15  | 1.389 (3) |
| N1—C22 | 1.465 (4)   | C14—H14  | 0.9500    |
| N1—C18 | 1.480 (4)   | C15—H15  | 0.9500    |
| N2—C17 | 1.448 (3)   | C16—H16A | 0.9800    |
| N2—C20 | 1.471 (3)   | C16—H16B | 0.9800    |
| N2—C19 | 1.478 (3)   | C16—H16C | 0.9800    |
| C1—H1A | 0.9800      | C17—C18  | 1.487 (4) |
| C1—H1B | 0.9800      | C17—H17A | 0.9900    |
| C1—H1C | 0.9800      | C17—H17B | 0.9900    |
| C2—H2A | 0.9800      | C18—H18A | 0.9900    |

|            |             |               |             |
|------------|-------------|---------------|-------------|
| C2—H2B     | 0.9800      | C18—H18B      | 0.9900      |
| C2—H2C     | 0.9800      | C19—H19A      | 0.9800      |
| C3—C4      | 1.393 (3)   | C19—H19B      | 0.9800      |
| C3—C8      | 1.394 (3)   | C19—H19C      | 0.9800      |
| C4—C5      | 1.389 (3)   | C20—H20A      | 0.9800      |
| C4—H4      | 0.9500      | C20—H20B      | 0.9800      |
| C5—C6      | 1.383 (3)   | C20—H20C      | 0.9800      |
| C5—H5      | 0.9500      | C21—H21A      | 0.9800      |
| C6—C7      | 1.380 (3)   | C21—H21B      | 0.9800      |
| C6—C9      | 1.514 (3)   | C21—H21C      | 0.9800      |
| C7—C8      | 1.392 (3)   | C22—H22A      | 0.9800      |
| C7—H7      | 0.9500      | C22—H22B      | 0.9800      |
| C8—H8      | 0.9500      | C22—H22C      | 0.9800      |
| C9—H9A     | 0.9800      |               |             |
| O1—In1—C1  | 106.45 (10) | C6—C9—H9C     | 109.5       |
| O1—In1—O2  | 78.32 (5)   | H9A—C9—H9C    | 109.5       |
| C1—In1—O2  | 108.82 (9)  | H9B—C9—H9C    | 109.5       |
| O1—In1—C2  | 107.23 (7)  | O2—C10—C11    | 122.42 (17) |
| C1—In1—C2  | 133.76 (11) | O2—C10—C15    | 120.24 (17) |
| O2—In1—C2  | 108.30 (8)  | C11—C10—C15   | 117.34 (17) |
| C3—O1—Li1  | 142.41 (15) | C10—C11—C12   | 120.8 (2)   |
| C3—O1—In1  | 121.02 (11) | C10—C11—H11   | 119.6       |
| Li1—O1—In1 | 96.57 (11)  | C12—C11—H11   | 119.6       |
| C10—O2—Li1 | 137.92 (16) | C13—C12—C11   | 121.9 (2)   |
| C10—O2—In1 | 125.00 (12) | C13—C12—H12   | 119.1       |
| Li1—O2—In1 | 94.94 (11)  | C11—C12—H12   | 119.1       |
| O1—Li1—O2  | 89.85 (15)  | C12—C13—C14   | 117.28 (18) |
| O1—Li1—N2  | 116.35 (17) | C12—C13—C16   | 122.0 (2)   |
| O2—Li1—N2  | 126.61 (19) | C14—C13—C16   | 120.7 (2)   |
| O1—Li1—N1  | 117.30 (18) | C13—C14—C15   | 121.4 (2)   |
| O2—Li1—N1  | 122.97 (18) | C13—C14—H14   | 119.3       |
| N2—Li1—N1  | 86.82 (15)  | C15—C14—H14   | 119.3       |
| C21—N1—C22 | 110.9 (3)   | C14—C15—C10   | 121.3 (2)   |
| C21—N1—C18 | 111.5 (3)   | C14—C15—H15   | 119.4       |
| C22—N1—C18 | 108.8 (2)   | C10—C15—H15   | 119.4       |
| C21—N1—Li1 | 105.9 (2)   | C13—C16—H16A  | 109.5       |
| C22—N1—Li1 | 116.8 (2)   | C13—C16—H16B  | 109.5       |
| C18—N1—Li1 | 102.62 (18) | H16A—C16—H16B | 109.5       |
| C17—N2—C20 | 111.9 (2)   | C13—C16—H16C  | 109.5       |
| C17—N2—C19 | 109.5 (2)   | H16A—C16—H16C | 109.5       |
| C20—N2—C19 | 107.9 (2)   | H16B—C16—H16C | 109.5       |
| C17—N2—Li1 | 103.99 (18) | N2—C17—C18    | 112.3 (2)   |
| C20—N2—Li1 | 109.79 (18) | N2—C17—H17A   | 109.1       |
| C19—N2—Li1 | 113.73 (18) | C18—C17—H17A  | 109.1       |
| In1—C1—H1A | 109.5       | N2—C17—H17B   | 109.1       |
| In1—C1—H1B | 109.5       | C18—C17—H17B  | 109.1       |
| H1A—C1—H1B | 109.5       | H17A—C17—H17B | 107.9       |



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|            |             |               |           |
|------------|-------------|---------------|-----------|
| In1—C1—H1C | 109.5       | N1—C18—C17    | 113.0 (2) |
| H1A—C1—H1C | 109.5       | N1—C18—H18A   | 109.0     |
| H1B—C1—H1C | 109.5       | C17—C18—H18A  | 109.0     |
| In1—C2—H2A | 109.5       | N1—C18—H18B   | 109.0     |
| In1—C2—H2B | 109.5       | C17—C18—H18B  | 109.0     |
| H2A—C2—H2B | 109.5       | H18A—C18—H18B | 107.8     |
| In1—C2—H2C | 109.5       | N2—C19—H19A   | 109.5     |
| H2A—C2—H2C | 109.5       | N2—C19—H19B   | 109.5     |
| H2B—C2—H2C | 109.5       | H19A—C19—H19B | 109.5     |
| O1—C3—C4   | 121.17 (17) | N2—C19—H19C   | 109.5     |
| O1—C3—C8   | 120.74 (17) | H19A—C19—H19C | 109.5     |
| C4—C3—C8   | 118.09 (17) | H19B—C19—H19C | 109.5     |
| C5—C4—C3   | 120.61 (17) | N2—C20—H20A   | 109.5     |
| C5—C4—H4   | 119.7       | N2—C20—H20B   | 109.5     |
| C3—C4—H4   | 119.7       | H20A—C20—H20B | 109.5     |
| C6—C5—C4   | 121.43 (19) | N2—C20—H20C   | 109.5     |
| C6—C5—H5   | 119.3       | H20A—C20—H20C | 109.5     |
| C4—C5—H5   | 119.3       | H20B—C20—H20C | 109.5     |
| C7—C6—C5   | 117.92 (18) | N1—C21—H21A   | 109.5     |
| C7—C6—C9   | 120.8 (2)   | N1—C21—H21B   | 109.5     |
| C5—C6—C9   | 121.2 (2)   | H21A—C21—H21B | 109.5     |
| C6—C7—C8   | 121.53 (18) | N1—C21—H21C   | 109.5     |
| C6—C7—H7   | 119.2       | H21A—C21—H21C | 109.5     |
| C8—C7—H7   | 119.2       | H21B—C21—H21C | 109.5     |
| C7—C8—C3   | 120.41 (19) | N1—C22—H22A   | 109.5     |
| C7—C8—H8   | 119.8       | N1—C22—H22B   | 109.5     |
| C3—C8—H8   | 119.8       | H22A—C22—H22B | 109.5     |
| C6—C9—H9A  | 109.5       | N1—C22—H22C   | 109.5     |
| C6—C9—H9B  | 109.5       | H22A—C22—H22C | 109.5     |
| H9A—C9—H9B | 109.5       | H22B—C22—H22C | 109.5     |

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