Backbone-Substituted $\beta$-Ketoimines and Ketoiminate Clusters: Transoid Li$_2$O$_2$ Squares and $D_2$-Symmetric Li$_4$O$_4$ Cubanes. Synthesis, Crystallography and DFT Calculations

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Abstract: The preparation and crystal structures of four $\beta$-ketoimines with bulky aryl nitrogen substituents (2,6-diisopropylphenyl and 2,4,6-trimethylphenyl) and varying degrees of backbone methyl substitution are reported. Backbone substitution “pinches” the chelate ring. Deprotonation with $n$-butyllithium leads to dimeric Li$_2$O$_2$ clusters, as primary laddered units, with an open transoid geometry as shown by crystal structures of three examples. The coordination sphere of each lithium is completed by one tetrahydrofuran ligand. NMR spectra undertaken in either C$_6$D$_6$ or 1:1 C$_6$D$_6$/$d_8$-THF show free THF in solution and the chemical shifts of ligand methyl groups experience significant ring-shielding which can only occur from aryl rings on adjacent ligands. Both features point to conversion to higher-order aggregates when the THF concentration is reduced. Recrystallization of the materials from hydrocarbon solutions results in secondary laddering as tetrameric Li$_4$O$_4$ clusters with a cuboidal core, three examples of which have been crystallographically characterised. These clusters are relatively insoluble and melt up to 250 °C; a consideration of the solid-state structures indicates that the clusters with 2,6-diisopropylphenyl substituents form very uniform ball-like molecular structures that will only be weakly solvated.

Keywords: $\beta$-ketoimine; $\beta$-ketoiminate; lithiation; high-nuclearity clusters; crystallography; DFT calculations; X-ray crystallography; multinuclear NMR; primary laddered units; secondary laddering

1. Introduction

Transition metal complexes of the deprotonated ligands derived from $\beta$-ketoimines 1 are of current interest in coordination chemistry and catalysis. Much of their use in catalysis has been in olefin polymerization [1,2]. Lanthanide alkoxydes stabilized by $\beta$-ketoimimates are active in ring-opening polymerization of lactones and lactides [3]. Some research has been done into other types of reactions [4], and metal complexes of $\beta$-ketoimines have been widely used as precursors for metalloorganic chemical vapour deposition (CVD) [5,6]. Much less is known about their main group metal derivatives, although $\beta$-ketoimimate complexes of aluminium are a notable exception [7,8]. A few magnesium complexes have also been studied with interest in their use as CVD precursors [9]. Alkali metal derivatives have been used as intermediates in the synthesis of transition metal complexes [10,11], but have not been extensively reported as isolated species [12–14].

The structural chemistry of lithiated organoelement species has seen enormous development over 30 years of active investigation and is known to show great diversity of structures due to aggregation...
and Lewis base coordination. Rings, ladders and higher aggregates have been obtained [15–18]. To date, there are several structurally characterised examples of lithium β-ketoiminates. Lithiation of 4-isopropylaminopent-3-en-2-one generates in presence of hexamethylphosphorhtriamide (hmpa) a transoid $\text{Li}_2\text{O}_2$ chelate dimer of type 2 (Cambridge Crystallographic Database, CSD, refcode NOWHUK) while in absence of the Lewis base an $\text{Li}_4\text{O}_4$ chelated tetrameric cubane (refcode: NOWHOW) of type 3 [12]. A fluorinated β-ketoiminate with a pendent $\text{Me}_2\text{N'}\text{CH}_2\text{CH}_2$ has been structurally characterised (refcode: XUZWOE) as a cisoid $\text{Li}_2\text{O}_2$ dimer with the $N'$ donors acting as an internal Lewis base [19], while a mixed copper-lithium ladder cluster was obtained from lithiated 1a and copper(II) chloride in toluene in which an oxygen from the copper chelate acts as “L” [20]. A similar $\text{Li}_2\text{O}_2$ cluster (refcode: SEKVIK) of a close analogue of ligand 1b (2,6-xylyl rather than Mes group) has two neutral ligands filling the coordination sphere of the lithium ions [21]. An iron(II) triflate complex derived from 1a (refcode: ISEXUA) has recently been structurally characterised [22]. Titanium chloride and chloromethyltin complexes (refcodes: LIRCAQ and DULREI) of 1b have also been structurally confirmed [23,24]. Similar chloroalkyltin complexes of 1c have been reported [25]. Main group element complexes of 1d have also been structurally characterised (GaCl₃, refcode: RUYSIO and SbCl₃, refcode: JOHQED) [26,27], as have complexes of this ligand with cobalt, copper and europium (refcodes: WUWDUO, WUWFAW, WUWFEA) [28].

As a continuation of our interest in heteroallyl ligands incorporating bulky substituents and their coordination chemistry [29–33], as well as in the structures and reactivities of $N'$-imidoylcarboximidamides [34,35], we now report crystal structures for two popular β-ketoimines 1a,b (Dipp = 2,6-diisopropylphenyl; Mes = 2,4,6-trimethylphenyl) (Scheme 1) [36] and the synthesis of two less-common analogues which have an additional methyl group at the “3” position of the heteropentadienes 1c,d. The structures of new transoid $\text{Li}_2\text{O}_2$ dimers 2a-c with L = THF and novel $D_2$-symmetric $\text{Li}_4\text{O}_4$ cubanes 3b-d are described. The relationship between dimeric and tetrameric aggregates and the preference for the common $S_4$- and rare $D_2$-symmetric $\text{Li}_4\text{O}_4$ cubanes is rationalised using hybrid-DFT calculations. We have recently reported the structure of the first mixed ketoiminate-alkyl complex of magnesium derived from 1b [37].

![Scheme 1. Identities of the title compounds.](image)

2. Results and Discussion

2.1. Synthesis, Structures and Tautomers of β-Ketoimines

The ketoimines 1c,d were prepared by the InBr₃-catalysed condensation of 3-methyl-2,4-pentandione with the corresponding anilines MesNH₂ or DippNH₂ [38] and have been fully characterised in the solid and in solution; previous reports of these ligands do not seem to have provided full details. The spectroscopic properties resemble those of the previously reported 1a,b [36]. The presence of the intramolecular H-bond is detected by broad resonances in the $^1\text{H}$ NMR at noticeably low frequencies (ranging from 11.8 to 13.2 ppm in CDCl₃ solution for the four exemplars) [39]. The presence in both 1a and 1c of two distinct $^1\text{Pr}$ methyl resonances suggesting that there is a lack of free rotation of the Dipp ring is also noteworthy. More interesting are the structures in the solid state.
which we have determined for all four species by single-crystal X-ray diffraction at low temperatures (see Figure 1 and Table 1). In each case, an NH hydrogen could be detected unambiguously in the difference Fourier map and their positions and isotropic temperature factors could be freely refined. This suggests that of the three theoretically possible tautomers (Scheme 2), all four ketoimines 1a–d are unambiguously in the enamine form B in the solid state.

![Scheme 2. Limiting tautomers for ketoimines: enol (A); enamine (B); or ketimine (C).](image)

The geometries of the three structure determinations match very well. This suggests that of the three theoretically possible tautomers (Scheme 2), all four ketoimines 1a–d are unambiguously in the enamine form B in the solid state.

The structure of 1a (Figure 1a) can be compared to that of (Z)-3-((2,6-diisopropylphenyl)amino)-1-phenylbut-2-en-1-one with which it shares an identical value for d(N–O) of 2.613(2) Å within experimental error (refcode NAWKUS [40]). The packing of this structure in regular sheets through weak intermolecular contacts is more symmetrical than that found in 1a. During this work, another crystal structure of 1a was published (refcode: UZOJOJ [25]). The geometries of the two structure determinations match closely.

| Parameter | 1a X-ray | 1a Calc. | 1b X-ray | 1b Calc. | 1c X-ray | 1c Calc. | 1d X-ray | 1d Calc. |
|-----------|---------|---------|---------|---------|---------|---------|---------|---------|
| O–C2      | 1.250(19)| 1.251   | 1.248(18)| 1.250   | 1.248(2)| 1.252   | 1.2489(17)| 1.252   |
| C2–C3     | 1.421(2) | 1.438   | 1.426(2)| 1.438   | 1.426(2)| 1.450   | 1.430(2)  | 1.450   |
| C3–C4     | 1.376(2) | 1.385   | 1.387(19)| 1.385   | 1.388(2)| 1.395   | 1.3872(19)| 1.395   |
| C4–N      | 1.3406(19)| 1.354  | 1.3395(18)| 1.385   | 1.349(2)| 1.358   | 1.3462(17)| 1.358   |
| C=N–C5    | 1.3406(19)| 1.354  | 1.3395(18)| 1.385   | 1.349(2)| 1.358   | 1.3462(17)| 1.358   |
| O1–C2–C3  | 123.16(14)| 123.50 | 122.99(13)| 123.47  | 123.69(16)| 123.98 | 123.35(12)| 123.99  |
| C2–C3–C4  | 123.22(14)| 123.04 | 123.26(13)| 123.07  | 120.18(14)| 120.40 | 120.59(12)| 120.46  |
| C3–C4–N   | 120.46(13)| 120.78 | 121.85(13)| 120.99  | 120.96(16)| 120.99 | 121.93(12)| 120.91  |
| C4–N–C6   | 127.46(13)| 126.85 | 124.92(12)| 126.46  | 120.8(13)| 128.03 | 126.29(11)| 128.37  |
| N–H       | 0.885(19) | 1.030  | 0.860(19)| 1.031   | 0.92(2) | 1.032   | 0.898(17) | 1.033   |
| N–H···O    | 2.6139(17)| 2.647  | 2.6571(16)| 2.652   | 2.5485(18)| 2.590 | 2.5823(15)| 2.591   |
| N–H···O'   | 141.9(16) | 138.8  | 133.71(16)| 138.2   | 140.9(19)| 140.1 | 140.0(15) | 140.4   |
| N–H···O''  | 2.984(16) |       | -       |         |         |       |         |         |

1 The atom numbering scheme is that shown in Figure 2d. 2 B3LYP/6-31G(d) hybrid DFT.

The structure of 1b (Figure 1b) is the sole exemplar in this set which shows additional intermolecular H-bonding to form centroymmetric dimers with respect to crystallographic centres of inversion in space group P21/n (see Figure A1 in Appendix A). The intramolecular d(N···O) value is 2.657(2) Å while between the two molecules it is 2.984(2) Å. This motif is strongly reminiscent of that found in 2-(2,6-diisopropylphenylamino)cyclohex-1-enyl phenyl ketone for which the corresponding values are: d(N···O) intra- 2.598(3) and 2.614(3); inter-molecular 3.205(3) and 3.206(3) Å. Thus, it is not the difference in steric bulk between the nitrogen substituents Dipp in 1a and Mes in 1b that determines these motifs, which are probably determined by crystal packing. During this work, two independent reports were published containing the same structure (refcodes: IFOWUW [41] and NABYEX [42]). The geometries of the three structure determinations match very well.

The isolated structure of 1c (Figure 1c) has a noticeably short d(N···O) value of 2.549(2) Å, 3% less than in 1a. Similarly, in 1d, d(N···O) is 2.582(2) Å, which is 3% less than in 1b. The origin of this “pinching-in” effect must lie with the additional backbone methyl group, such that there
are three methyl groups in series along the ketoimine backbone. Although methyl groups are not considered bulky substituents, local steric pressure can be generated even by relatively small groups in close proximity [43]. Of about 150 crystal structures of β-ketoimines in the CSD, excluding those cases where two or more of the hetero-pentadiene atoms are constrained within rings, none bear a 3-methyl substituent and only three examples of substitution are found (refcodes: JEKLUA, JEMMAO, and SENBAO), each of which is a perpendicularly-oriented acyl group that is not expected to develop much steric pressure [44,45].

![Displacement ellipsoids plots (40% probability) of the molecular structures of the ketoimine ligand precursors as found in the respective crystal structures: (a) Ligand 1a; (b) ligand 1b; (c) ligand 1c; and (d) ligand 1d. The atom numbering schemes are indicated.](image)

In the extended structure of 1c, the ketoimine chains form into planes that lie along the (020) Miller planes with only weak intermolecular contacts. The observed H-bonding is strictly intramolecular. The same is true of 1d, but the crystal packing of this exemplar has the molecules arranged such that the aromatic mesityl rings of pairs of molecules are parallel-displaced edgewise at close to the ideal distances for a π–π stacking interaction [46], 3.546 Å from the centre of one mesityl to the plane made by the other and with an average edgewise displacement of 1.337 Å.

For all these β-ketoimines the H-bonded pseudo six-member rings are rigorously planar and there is a degree of bond averaging suggestive of at least partly-delocalized π-electrons with sp²-hybridized 2nd-row elements (Table 1). Thus, the C–N bonds are considerably shorter than expected for a single bond (Av. 1.339 Å) while the formal C=C double bond (Av. 1.316 Å) prescribed by the enamine structure is significantly shorter than that found. Similarly, the formal C–C single bond (Av. 1.530 Å) is not observed; instead the value is typical of single bonds in conjugated systems (Av. 1.460 Å), while the C=O bond is longer than normal values for ketones (Av. 1.210 Å) [47].

The geometry of these structures is accurately reproduced by (gas phase) B3LYP/6-31G(d) calculations (Table 1) except for the C(2)–C(3) distances in 1c,d which are overestimated by 0.02 Å. The DFT calculations closely replicate the shortening of d(N···O) by ~0.1 Å, supporting the notion that steric crowding of the backbone methyl groups causes the ring to pinch in. Recent computational
studies on a model β-ketoimine 1 with substituents R₁ = R₂ = R₄ = CH₃; R₂ = H provides strong support for the preference for the enamine tautomer and moreover has demonstrated that the main factor favoring the enamine is promotion of planarity of the N atom so that its lone pair can be part of a delocalized π-system [48].

2.2. Synthesis and Structures of Ketoiminate Lithium Complexes

The neutral lithium complexes formed by deprotonation of 1a–d with "BuLi fall into two broad classes: 2a–c which are prepared in and crystallised from THF-hexane mixed solvents and which retain coordinated THF; 3b,c which are prepared in heptane-hexane mixed solvents and which crystallise as unsolvated species. In this system, 3d stands out in that it preferentially crystallises as the unsolvated cluster even in presence of THF. X-ray quality crystals of 2a–c and 3d form on cooling from a THF-enriched solution; 3b recrystallizes from hot toluene, and 3c from hot heptanes.

2.2.1. Transoid Li₂O₂ Clusters

Each of the THF solvates 2a–c consists of a ketoiminate chelated Li⁺ ion further coordinated by one THF perpendicular to the chelate ring (Figure 2 and Table 2); these rings associate into crystallographically centrosymmetric dimers with central Li₂O₂ squares that are close to symmetrical with the “inter-monomer” Li–O distances (2a 1.917(4); 2b 1.948(3); 2c 1.898(2) and 1.908(2) Å) only 1%–3% longer than the “intra-monomer” (2a 1.899(3); 2b 1.888(3); 2c 1.868(3) and 1.867(2) Å) values. The result is that each Li⁺ ion is tetracoordinate but with angles severely distorted from tetrahedral values. There are no significant short contacts between any of these butterfly clusters within their unit cells. For 2c, the lattice has two crystallographically independent “monomers” in the asymmetric unit, each of which is dimerized on a lattice inversion centre. The two resultant dimers, which are crystallographically distinct, have very comparable geometric parameters and only one example is shown in Figure 2c.

Table 2. Experimental ¹ and calculated ² bond lengths (Å) and angles (°) for 2a–d.

| Parameter | 2a X-ray | 2a Calc. | 2b X-ray | 2b Calc. | 2c X-ray | 2c Calc. | 2d X-ray | 2d Calc. |
|-----------|---------|---------|---------|---------|---------|---------|---------|---------|
| O–C₂      | 1.286(19) | 1.290   | 1.283(2) | 1.291   | 1.284(1) | 1.289   | 1.292   |         |
| C₂–C₃     | 1.372(2)  | 1.390   | 1.377(2) | 1.390   | 1.385(4) | 1.403   | 1.402   |         |
| C₃–C₄     | 1.431(2)  | 1.437   | 1.432(2) | 1.435   | 1.450(1) | 1.451   | 1.451   |         |
| C₄–N      | 1.301(2)  | 1.312   | 1.306(2) | 1.312   | 1.307(0) | 1.317   | 1.315   |         |
| C₂–C₃     | 1.523(2)  | 1.524   | 1.523    |         | 1.524    |         |         |         |
| Li–N      | 2.021(3)  | 2.065   | 2.016(3) | 2.022   | 2.023(2) | 2.041   | 2.007   |         |
| Li–O chelate | 1.899(3) | 1.912   | 1.888(3) | 1.902   | 1.868(1) | 1.882   | 1.881   |         |
| Li–O bridge | 1.917(3) | 1.939   | 1.948(3) | 1.960   | 1.903(7) | 1.947   | 1.947   |         |
| Li–O(THF) | 1.988(3)  | 2.040   | 1.991(3) | 2.016   | 1.98(2)  | 2.037   | 2.026   |         |
| O–C₂–C₃   | 125.34(16) | 125.76  | 125.57(16) | 125.81  | 125.47(4) | 125.47  | 125.32  |         |
| C₂–C₃–C₄  | 128.68(16) | 128.79  | 128.08(16) | 128.20  | 123.66(11) | 124.11  | 123.75  |         |
| C₃–C₄–N   | 122.86(15) | 123.90  | 123.40(16) | 123.50  | 123.66(15) | 124.15  | 123.82  |         |
| C₄–N–C₆   | 120.58(14) | 121.48  | 118.78(14) | 122.10  | 120.76(9)  | 121.76  | 122.27  |         |
| O–Li–N    | 95.96(13)  | 96.58   | 96.49(13) | 97.03   | 92.28(6)  | 92.98   | 92.99   |         |
| Li–O–Li   | 85.89(13)  | 85.76   | 86.52(13) | 85.57   | 88.1(15)  | 86.73   | 85.74   |         |
| O–Li–O    | 94.11(13)  | 94.24   | 93.48(13) | 94.43   | 92.0(15)  | 93.27   | 94.26   |         |
| O–Li–O(THF)| 107.6(11) | 107.81  | 112(9)    | 111.02  | 108(3)    | 108.96  | 112.06  |         |

¹ The atom numbering scheme is that shown in Figure 2d. ² B3LYP/6-31G(d) hybrid DFT.
The influence of the extra backbone methyl group in 2c is evident in these lithiated derivatives just as is the case for 1c,d. Thus, the $d(N\cdots O)$ values of 2.805(1) and 2.809(1) Å are 4% shorter than those that pertain in 2a, 2.913(2) and 2b, 2.914(2) Å, due to “pinching in” of the chelate ring. This can also be seen by the fact that the Li atom is twice as far out of the chelate ring ligand least-squares plane (0.44 Å) compared to 2a (0.24 Å). Upon coordination to Li$^+$, the bond lengths within the ketoiminate ligands change in predictable fashion. Thus, the C–O distances lengthen ~3%, C–C shorten by ~4%, C–C lengthen by ~4% and C–N shorten by ~3%. All these changes are consistent with conversion from a limiting enamine geometry B towards a delocalized chelate ring.

There are several comparable Li$_2$O$_2$ butterfly complexes of ketoiminate ligands in the literature. The most comparable structures to 2a–c are the all-aliphatic complex bis((µ$_2$-N-isopropyl-2,4-dimethyl-1-oxa-5-azapenta-2,4-dienyl)-hexamethylphosphoramido-lithium (refcode: NOWHUC) which has hmpa oxygen donors in place of THF [12] and three closely similar bis(µ$_2$-3-((aryl)iminio)-1-phenylbut-1-en-1-oxo)-bis(tetrahydrofuran)-di-lithium complexes reported by Liu et al. (refcodes: SIYDAH, SIYDEL, SYDIP) [14]. In NOWHUC, the intra- (1.892) and inter-“monomer” (1.955 Å) Li–O distances are most similar to those in 2b. In the structure of a 2,6-xylyl ketoiminate a structure very similar to that in 2b is found (refcode: SEKVIP) [21]. In place of the two THF molecules, two neutral ligand molecules are coordinated to lithium ions via the carbonyl oxygen donors. The dimensions in this structure are very close to those in 2b, except for the Li–O distances which are longer (0.024 Å) for the ligand O and shorter for the exocyclic value (0.012 Å).
2.2.2. “Tetrameric” Cuboidal Clusters

All three cubane complexes 3b–d adopt the same basic geometry with minor distortions in which the core geometry has approximate $D_2$ point-group symmetry (Figure 3a). The CSD reports 21 Li$_4$O$_4$ cuboidal clusters with nitrogen donors coordinated to Li. Seven of these are either non-chelating or have higher denticity. Of the remainder, eleven adopt the $S_4$ geometry while only two have the $D_2$-symmetric structure (Scheme 3).

Figure 3. Displacement ellipsoids plots (40% probability) of the tetrameric molecular structures of cuboidal Li$_4$O$_4$ ketoiminate clusters as found in their crystal structures: (a) common cuboidal core with ipso carbon of the aromatic groups coloured brown; (b) cluster 3b; (c) cluster 3c; and (d) cluster 3d. The atom numbering schemes are shown. H atoms on C have been omitted to enhance visualization of the clusters. A disordered, uncoordinated toluene molecule present in the lattice of 3b has been omitted and solvent presumed to be heptane was removed from the structure of 3c using the “SQUEEZE” method.

The structure observed in 3b (Figure 3b and Table 3) is remarkably symmetrical with all the ligand substituents oriented as required by the point group. Two Mes rings attached at opposite corners of the cube are directed away from the cube face and the other two face the opposite direction, each set creating a cavity which in the lattice provide spaces for solvent molecules (toluene). The Li$_4$O$_4$ faces perpendicular to the $D_2$ principal axis are almost square, while the four parallel faces are distinctly
rhomboidal ($\angle \text{Li–O–Li} \sim 83^\circ$). The Li–O distances parallel to the principal axis are precisely those chelated by the ketoiminate ligand and have a mean length of 1.924(5) Å. This is about 3% shorter than the mean Li–O distances for the eight bonds that are not chelated at 1.976(10) Å.

The structure of 3c (Figure 3c) has the most congested ligand 1c, with Dipp groups on nitrogen as well as the extra backbone methyl substituent. The same basic high-symmetry geometry is adopted as found for 3b but the “square” face perpendicular to the principal axis is distinctly distorted into an envelope conformation. This results in the structure being overall much squatter than of the previous example, and not just because of the absence of the substituents at position 4 on the aromatic rings. Here too the four chelated Li–O distances (mean value, 1.874(3) Å) are shorter (by 7%) than the eight bridging distances (mean value, 2.01(4) Å). However, the chelate rings remain close to planar with only a very small deviation of Li out of the average chelate planes. The crystal packing leads to smaller voids but these appear to contain disordered heptane molecules (NMR evidence) which we could not model accurately and which in the end were excluded from the electron-density maps.

| Parameter | 3a | 3b | 3c | 3d |
|-----------|----|----|----|----|
| O–C–2     | 1.305 | 1.303(2) | 1.306 | 1.310(2) | 1.310 | 1.307 | 1.310(3) | 1.308 | 1.308 |
| C–C–3     | 1.378 | 1.366(2) | 1.382 | 1.370(3) | 1.392 | 1.395 | 1.374(1) | 1.392 | 1.394 |
| C–C–4     | 1.443 | 1.440(2) | 1.442 | 1.460(7) | 1.464 | 1.461 | 1.454(2) | 1.458 | 1.457 |
| C–N–4     | 1.311 | 1.302(3) | 1.308 | 1.309(2) | 1.314 | 1.318 | 1.309(4) | 1.312 | 1.314 |
| Li–N      | 2.078 | 1.988(4) | 2.002 | 2.012(5) | 2.056 | 2.036 | 1.968(12) | 1.983 | 2.003 |
| Li–O chelate | 1.914 | 1.924(5) | 1.931 | 1.874(3) | 1.878 | 1.881 | 1.903(15) | 1.897 | 1.887 |
| Li–O bridge | 2.026 | 1.976(10) | 1.997 | 2.01(4) | 2.046 | 2.049 | 1.982(1) | 2.014 | 2.036 |
| O–C–2     | 125.1 | 125.15(16) | 125.3 | 124.8(4) | 124.9 | 124.91 | 125.2(3) | 125.3 | 125.5 |
| C–C–3     | 129.1 | 127.82(37) | 128.9 | 124.0(3) | 124.1 | 125.32 | 123.9(6) | 124.4 | 124.7 |
| C–C–4     | 124.3 | 122.77(24) | 123.6 | 123.5(3) | 124.8 | 124.96 | 123.3(3) | 123.8 | 124.1 |
| C–N–4     | 120.7 | 120.29(98) | 121.5 | 119.3(11) | 120.8 | 120.58 | 121(1) | 122.0 | 121.4 |
| Li–N      | 96.0  | 94.77(71) | 97.3  | 91.3(4)  | 92.3  | 96.08 | 92.7(5)  | 93.9  | 94.7 |
| Li–O–Li   | 87.7  | 85.7(19)  | 85.8  | 86(3)    | 86.5  | 87.37 | 84.8(14) | 85.4  | 85.0 |
| O–Li–O    | 91.9  | 94(2)     | 94.0  | 94(3)    | 93.2  | 92.57 | 95.0(15) | 94.4  | 94.0 |
| C–N–Li    | 120.3 | 124.1(6)  | 121.7 | 125.7(4) | 123.6 | 119.91 | 123.9(9) | 124.8 | 122.7 |
| C–O–Li    | 125.1 | 125.1(8)  | 123.1 | 130.2(4) | 130.0 | 126.04 | 125(3)   | 127.2 | 125.9 |

The structure of 3d (Figure 3d) is the most distorted of the three by a significant margin. The lithium atoms are distinctly out of the best plane of the ligand atoms, either causing or the result of twisting of the chelate rings. However, here too the four chelated Li–O distances (mean value, 1.903(15) Å) are shorter than the bridging Li–O distances (mean value, 1.982(2) Å) but the difference is only 4%. The chelate rings are twisted away from the principal axis which allows for a smaller ligand bite angle and consequently the Li atoms are 0.494 Å out of the least squares plane generated by the five chelate ring atoms.

The shorter $d(\text{N}–\text{O})$ values for the clusters derived from the backbone-methyl ligands 1c,d are maintained in the cubane clusters. Thus, the average $d(\text{N}–\text{O})$ value in 3b is 2.878(13), in 3c 2.780(7) and 3d 2.800(2) Å, which is again shorter by about 3%–4% when using the methylated ligands. Unsurprisingly this is reflected in a smaller average N–Li–O bite angle for the methylated ligands. The bond distances within the chelate rings in 3b–d become even more averaged than in 2a–c. The O–C2 distances are noticeably longer, presumably because the oxygen is now donating to three lithium ions in the cubane. The geometrical parameters are very well simulated in the DFT calculations, which provides substantial confidence that 3a, for which no crystal structure was obtained, will have a similar geometry.

There are two previously reported ketoiminate Li4O4 cluster structures in the CSD. Tetrakis($\mu_3$-N-isopropyl-2,4-dimethyl-1-oxa-5-azapenta-2,4-dienyl)-tetralithium (refcode: NOWHOW)
adopts the $S_4$-symmetric geometry \[12\], while tetrakis($\mu_3$-4-((3-methoxyphenyl)imino)pent-2-en-2-olato)-tetra-lithium (refcode: WUQFAR) adopts the $D_2$ geometry as observed for 3b–d \[13\]. These clusters also possess shorter average Li–O distances within the chelate rings (1.905(5) and 1.915(5) Å, respectively) than for the bridging bonds (2.00(2) and 1.961(1) Å).

**Scheme 3.** Dimerization paths of the transoid rings of 2 to achieve the known limiting cubane geometries with $D_2$ or $S_4$ symmetry. Note that 3b–d all adopt the $D_2$ geometry.

2.3. Formation and Isomer Selection of Li$_4$O$_4$ Clusters

Conceptually, the clusters, whether they adopt the observed $D_2$ or the much more commonly observed $S_4$ geometry in the tetramers, are the results of combining the molecular squares discussed above for 2a–c—the primary laddered units \[18\]—as diagrammed in Scheme 3. Since the dimers are all transoid, the face to face combination requires not only the displacement of the two coordinated THF molecules (“L” in Scheme 3) but also folding back of one of the two chelate rings because the observed cubane structures contain cisoid rings. The possible final geometries are obtained from the Li$_2$O$_2$ squares by combining two cisoid rings face-to-face, either in register (top) resulting in $D_2$, or out of register (bottom) yielding $S_4$. The evidence from synthesis is that formation of the cuboidal clusters is suppressed in THF solution but becomes more favourable on reducing the mole fraction of the coordinating solvent. Note also that the formation of each cubane releases four equivalents of THF, suggesting a likely entropic driving force for the forward reaction.

The evidence from solution NMR obtained in C$_6$D$_6$ or 1:1 C$_6$D$_6$/THF-$d_8$ mixtures shows chemical shifts for free THF for 2a–c. Moreover, the NMR spectra of 2b and 3b in C$_6$D$_6$ are identical. This suggests that in these solvents, the formation of the $D_2$ cuboidal clusters is favoured. It is furthermore the case that both 3a and 3c (in which the aromatic group on N is Dipp) are insoluble in C$_6$D$_6$ but soluble in the mixed solvent. By contrast, 3b and 3d (with Mes on N) dissolve in C$_6$D$_6$. This is contrary to the behaviour of most Dipp compounds, which tend to be very soluble in hydrocarbon solvents. To explain this anomaly, space filling models of the two types of cluster were examined (see Figure A2 in Appendix A). These show a very clear difference in molecule structure, with the Dipp-based structures adopting a very compact spheroidal geometry possessing a very smooth surface that may be difficult to solvate, whereas the Mes-based complexes have large clefts that could be accessed by benzene solvent molecules, aiding solvation.

For confirmation of the hypothesis that the solution forms for all four complexes are the cuboidal Li$_4$O$_4$ geometry, consider the coordination chemical shifts for the C1 and C5 methyl groups (see labels in Figure 2d). The C1 methyl group ($\beta$ to the oxygen atom in the ligand) is shifted to higher frequency by from 0.41 to 0.56 ppm, whereas the C5 group ($\beta$ to the nitrogen atom) changes little from the free-ligand values. A consideration of the geometries of the transoid Li$_2$O$_2$ square and cuboidal Li$_4$O$_4$ structures indicates that only in the latter do the C1 methyl groups experience significant
ring-shielding from the aryl rings of an adjacent ketoiminate ligand (methyl carbon to ring-centroid distances average in the solid-state structures to 4.557 (3b), 4.432 (3c) and 3.881 (3d) Å. Both the distances and the orientation of the aromatic rings in the transoid dimers are markedly less favourable for ring-shielding. Very similar effects and geometrical factors apply for the five-coordinate aluminium bis ketoiminates reported by Yu et al. [7]. In four structurally characterised complexes of ligands 1a,b with methyl, ethyl, chloro and fluoro-aluminiums (refcodes BAMFAX, BAMFEB, BAMFIF and BAMFOL, respectively) the average methyl carbon to ring-centroid distances are 3.903, 3.927, 3.904 and 3.912 Å; the corresponding Δδ are +1.17, +1.17, +1.21 and +1.21 ppm (see representative structure diagrams in Figure A3 in Appendix A). The larger ring-shielded shifts are consistent with the short distances and a more favourable orientation over the ring centres in these structures compared to 3b–d. Note that, by contrast, the monomeric dialkylaluminium complexes of ligand 1a also reported by Yu et al., which cannot experience ring shielding, show no upfield shift compared to the free ligands in the same solvent [7]. The 7Li NMR evidence is less conclusive than that obtained from 1H, although possible time-scale differences make comparisons difficult. There is only one lithium resonance in each case, and the frequencies are quite similar. For the samples measured in 1:1 C6D6/THF-d8, mixture, sharp singlets are observed around +2.5 ppm (2a, 2c, 3b) but samples in pure C6D6 can be sharp (2b/3b) or very broad (2c, 3d). Low solubility appears to strongly affect the latter two spectra. Overall, though the presence of 2 ↔ 3 exchange for samples which contain THF cannot be excluded, the dominant species as judged from the 1H NMR signals (C1 methyl and THF peaks) appear to be 3.

Relatively simple DFT calculations (B3LYP/6-31G(d)) in the gas-phase were undertaken to help explain the observed chemistry. Good matches could be obtained for the geometries of all the ligands and complexes, and the geometries of the missing complexes (2d, 3a) were included computationally (see results compiled in Tables 1–3). Using these computed structures, the energetics of the conversions of 2 to 3 in the gas phase were computed. The outcomes favour 2 over 3 by 104, 99, 133 and 70 kJ·mol⁻¹ for a–d, respectively. Evidently these results do not agree with experiment; the inclusion of solvation energies might change these results, but also the entropy associated with the release of THF molecules in the formation of 3 may be significant.

DFT was also used to help explain the preference for the D2 over the S4 geometry for the cuboidal clusters 3. Such calculations were only undertaken for 3c,d and the corresponding S4 structures 3c' and 3d'. Representative results are shown in Figure 4; the energies calculated for 3c' and 3d' are 23 and 41 kJ·mol⁻¹ higher than for 3c and 3d. A consideration of the optimized computed structures suggests that the origin of the difference is steric as there are significant steric clashes in the S4 structures that are absent in the preferred D2 geometries (see Scheme 4).

![Figure 4. DFT calculated structures of 3c: (a) in the crystallographically determined D2 geometry; and (b) in the alternate S4 geometry (3c'). Hydrogen atoms are omitted.](image-url)
were used to assist with assigning the carbon NMR signals where needed. 1H NMR are referenced to tetramethylsilane (TMS), 13C NMR are referenced to CDCl3 or C6D6 and 7Li NMR are referenced to an external 9.7 mol/kg LiCl in D2O solution; coupling constants are expressed in Hz. X-ray crystal data were collected on a Bruker Smart Apex II, with solution and refinement using the Shelxtl software package. Mass spectra was obtained using a Varian 4000 GC/MS/MS (Palo Alto, CA, USA). Elemental analyses were obtained using an Elementar analyser. Infrared spectra were recorded on a Bruker Alpha-P diamond ATR spectrometer (East Milton, ON, Canada) as neat samples. 1H, 13C, and 7Li NMR spectra were recorded on a Bruker AvanceII spectrometer operating at 300.13, 75.47 and 116.64 MHz, respectively. HSQC and HMBC were used to assist with assigning the carbon NMR signals where needed. The ketoimines were synthesized by the literature methods [38]. In a round bottom flask 5.00 g (43.5 mmol) of 3-methyl-2,4-pentandione, 8.85 g (43.5 mmol) 2,6-Diisopropylaniline, 2,4,6-trimethylaniline, 2,4-pentanedione, 3-methyl-2,4-pentandione, indium tribromide, 1.6 M n-butyl lithium in hexane (Aldrich, Saint Louis, MO, USA), aluminium chloride (Merck, Kenilworth, NJ, USA), and benzene-d6 (CDN Isotopes 0.8 mL ampules) were used as received. Solvents were reagent grade, or better, and were used as received (methanol, hexanes, pentane, chloroform), distilled from sodium/benzophenone (tetrahydrofuran), or obtained from an MBraun Solvent Purification System (heptane, toluene, benzene, methylene chloride). Infrared spectra were recorded on a Bruker Alpha-P diamond ATR spectrometer (East Milton, ON, Canada) as neat samples. 1H, 13C, and 7Li NMR spectra were recorded on a Bruker AvanceII spectrometer operating at 300.13, 75.47 and 116.64 MHz, respectively. HSQC and HMBC were used to assist with assigning the carbon NMR signals where needed. 1H NMR are referenced to tetramethylsilane (TMS), 13C NMR are referenced to CDCl3 or C6D6 and 7Li NMR are referenced to an external 9.7 mol/kg LiCl in D2O solution; coupling constants are expressed in Hz. X-ray crystal data were collected on a Bruker Smart Apex II, with solution and refinement using the Shelxtl 6.14 software package. Mass spectra was obtained using a Varian 4000 GC/MS/MS (Palo Alto, CA, USA). Elemental analyses were obtained using an Elementar Vario Micro Cube (Langenseelbold, Germany). The ketoimines 1a,b were synthesized by the literature methods [38].

3. Materials and Methods

3.1. General Methods

All experimental procedures were performed under a nitrogen atmosphere using modified Schlenk techniques, unless otherwise noted. 2,6-Diisopropylaniline, 2,4,6-trimethylaniline, 2,4-pentanedione, 3-methyl-2,4-pentandione, indium tribromide, 1.6 M n-butyl lithium in hexane (Aldrich, Saint Louis, MO, USA), aluminium chloride (Merck, Kenilworth, NJ, USA), and benzene-d6 (CDN Isotopes 0.8 mL ampules) were used as received. Solvents were reagent grade, or better, and were used as received (methanol, hexanes, pentane, chloroform), distilled from sodium/benzophenone (tetrahydrofuran), or obtained from an MBraun Solvent Purification System (heptane, toluene, benzene, methylene chloride). Infrared spectra were recorded on a Bruker Alpha-P diamond ATR spectrometer (East Milton, ON, Canada) as neat samples. 1H, 13C, and 7Li NMR spectra were recorded on a Bruker AvanceII spectrometer operating at 300.13, 75.47 and 116.64 MHz, respectively. HSQC and HMBC were used to assist with assigning the carbon NMR signals where needed. 1H NMR are referenced to tetramethylsilane (TMS), 13C NMR are referenced to CDCl3 or C6D6 and 7Li NMR are referenced to an external 9.7 mol/kg LiCl in D2O solution; coupling constants are expressed in Hz. X-ray crystal data were collected on a Bruker Smart Apex II, with solution and refinement using the Shelxtl 6.14 software package. Mass spectra was obtained using a Varian 4000 GC/MS/MS (Palo Alto, CA, USA). Elemental analyses were obtained using an Elementar Vario Micro Cube (Langenseelbold, Germany). The ketoimines 1a,b were synthesized by the literature methods [38].

3.2. Synthesis of Ketoimines

3.2.1. 4-((2,6-Diisopropylphenyl)amino)-3-methyl-3-methyl-pent-3-en-2-one 1c

In a round bottom flask 5.00 g (43.5 mmol) of 3-methyl-2,4-pentandione, 8.85 g (43.5 mmol) 2,6-diisopropylaniline, and 0.154 g (0.435 mmol) of InBr3 were combined and allowed to stir overnight. The cloudy solution was then diluted with 60 mL of distilled water, extracted 3 times with 25 cm3 of ethyl acetate, the organic layers combined and then dried with magnesium sulphate. The solvent was removed under reduced pressure to give colourless solid and orange liquid. The solid was filtered off and recrystallized from hexanes giving pale yellow plates of 1c (2.063 g, 17.3%). M.p. 122–129 °C; (Found: C, 78.5; H, 9.6; N, 5.1. C18H27NO requires C, 78.7; H, 9.7; N, 5.4%); νmax(neat)/cm−1: 2960s, 2924m, 2867m, 1598vs, 1555vs, 146 4s, 1422s, 1384s, 1352vs, 1262vs, 1235s, 1169s, 1099m, 1053m, 966vs, 814vs, 776vs, 709s, 590m, 445m, 414m. NMR δ(1H, CDCl3, 25 °C): 13.18 (1 H, br s, NH), 7.28 (1H, t, J = 7.44, para CH), 7.17 (2H, d, J = 7.44, meta CH), 3.01 (2 H, sept, J = 6.87, CHCH3), 2.24 (3 H, s, CH3C(O)C), 1.92 (3 H, s, C(O)C(CH3)2), 1.70 (3 H, s, C(NDipp)CH3), 1.18 (6 H, d, J = 6.87, CHCH3), 1.14
(6H, d, J 6.87, CHCH3). δ (13C, CDCl3, 25 °C): 196.02 (C=O), 161.83 (C−N), 146.46 (C_ortho), 134.59 (C_ipso), 127.96 (C_para), 123.62 (C_meta), 98.79 (C(O)(CH3)C), 28.69 (CH3C(O)C), 28.62 (CHCH3), 24.65 (CHCH3), 22.91 (CHCH3), 16.72 (C(NDipp)CH3), 14.98 (C(O)C(CCH3)) ; m/z (El) 273 (M+, 18%), 202 (DippNCCH3+, 100%), 187 (DippNC+, 24%), 160 (C12H16, 20%).

3.2.2. 4-((2,4,6-Trime)thylphenylamino)-3-methyl-pent-3-en-2-one 1d

Procedure as for 1c from 5.00 g (43.5 mmol) of 3-methyl-2,4-pentanedione, 5.88 g (43.5 mmol) of 2,4,6-trimethylalanine, and 0.154 g (0.4344 mmol) InBr3; removal of the solvent gave an orange liquid from which crystals formed after 2 days. The solid was filtered off and recrystallized from hexanes to give faintly orange plates of 1d (3.619 g, 36.0%). M.p. 64–68 °C; (Found: C, 77.7; H, 8.8; N, 6.1. C_{15}H_{21}NO requires C, 77.4; H, 8.8; N, 6.4%; \gamma_{max}(neat)/cm^{-1}: 2947w, 2914w, 2859w, 1595s, 1538vs, 1487s, 1435m, 1417m, 1387m, 1367m, 1263vs, 1198s, 1147w, 967vs, 884m, 857s, 814m, 760 m, 696m, 588m, 532w, 482m. NMR δ (H, CDCl3, 25 °C): 12.99 (1H, br s, NH), 6.89 (2H, s, CH), 2.28 (3H, s, CH3). 2.13 (6H, s, ortho CH3), 1.91 (3H, s, C(O)CCCH3), 1.70 (s, 3H; CH3 on C(NMes)CH3), δ (13C, CDCl3, 25 °C): 195.91 (C=O), 161.60 (C−N), 136.57 (C_para), 135.80 (C_ipso), 134.91 (Cortho), 128.92 (Cmeta), 98.85 (C(O)(CH3)C(NMes), 28.60 (CH3C(O)C), 21.02 (para CH3), 18.40 (ortho CH3), 16.03 (C(NMes)CH3), 14.92 (C(O)CCH3); m/z (El) 232 (MH+, 100%), 231 (M+, 30%), 160 (MesNCCH3+, 10%).

3.3. Synthesis of the Ketoimide Lithium Complexes

3.3.1. Lithium Ketoimide Complex 2a

A solution of 1.006 g (3.878 mmol) of 1a in 8 mL of dry THF in a Schlenk tube was cooled in an ice/salt bath and 2.5 mL (4.000 mmol) of 1.6 M BuLi in hexanes to give faintly orange plates of 2a (0.322 g, 24.6%) suitable for X-ray crystallography. M.p. 229–230 °C, dec. 270 °C. NMR δ (H, 1:1 THF(C6D5), 25 °C): 1:10 ligand:THF: 7.11 (2H, d, J = 7.25, meta CH), 7.02 (1H, t, J = 7.25, para CH), 4.82 (s, 1H; backbone CH), 3.59 (122 H, m, THF), 3.16 (2H, septet, J = 6.82, CHCH3), 1.66 (s, 3 H, CH3C(O)C), 1.61 (122 H, m, THF), 1.55 (3 H, s, C(NDipp)CH3), 1.19 (6 H, d, J = 6.82, CHCH3), 1.14 ppm (6 H, d, J = 6.82, CHCH3). δ (13C, 1:1 THF(C6D5), 25 °C): 178.48 (C−O), 168.22 (CN), 148.84 (C_ipso), 140.32 (Cortho), 123.72 (Cpara), 123.52 (Cmeta), 96.51 (backbone CH), 28.60 (CH3C(O)C), 28.17 (CHCH3), 24.64 (CHCH3), 24.56 (CHCH3), 23.09 (C(NDipp)CH3). δ (Li, 1:1 THF(C6D5), 25 °C): 2.14.

3.3.2. Lithium Ketoimide Complex 2b

Procedure as for 2a from 1.005 g (4.624 mmol) of 1b in 9 mL of THF and 3.0 mL (4.800 mmol) of 1.6 M BuLi in hexanes to give colourless plates of 2b (0.440 g, 31.2%) suitable for crystallography. M.p. 272–274 °C dec. NMR δ (H, C6D5, 25 °C): 6.84 (2H, s, CH meta), 5.02 (1H, s, CH mesityl), 3.57 (m, 5H, THF), 2.20 (3H, s, para CH3), 2.11 (6H, s, ortho CH3), 1.52 (3H, s, ligand CH3), 1.49 (3H, s, ligand CH3), 1.41 (5H, m, THF). δ (13C, C6D5, 25 °C): 176.27 (C−O), 169.14 (C=N), 147.41, 138.22, 132.35, 129.66, 129.28, 128.56, 128.25, 126.03, 99.20 (backbone CH), 28.30 (CH3−CO), 22.00 (para−CH3), 21.76 (CH3 toluene), 21.32 (CH3−CN), 18.52 (ortho−CH3). δ (Li, C6D5, 25 °C): 2.76 ppm.

3.3.3. Lithium Ketoimide Complex 2c

Procedure as for 2a from 0.930 g (3.40 mmol) of 1c in 10 mL of THF, and 2.2 mL (3.5 mmol) of 1.6 M BuLi in hexanes to give colourless blocks of 2c (0.333 g 13.9%) suitable for crystallography. m.p. 139–145 °C. NMR δ (H, 1:1 THF(C6D5), 25 °C, containing 1:26 ligand:THF) 7.10 (2H, d, J 7.49, meta CH), 7.00 (1H, t, J 7.49, para CH), 3.59 (106 H, m, THF), 3.11 (2H, sept, J 6.86, CHCH3), 1.85 (3 H, s, C(O)(O)CH3), 1.74 (3 H, s, CH3C(O)C), 1.68 (3 H, s, C(NDipp)CH3), 1.63 (106 H, m, THF), 1.16 (6 H, d,
A solution of 0.997 g (4.59 mmol) of 1b in 10 mL of heptane at 0 °C was treated with 3.0 mL (4.8 mmol) of 1.6 M BuLi in hexanes and then heated to 70 °C to dissolve all solids. After removal of solvent in vacuum, the residue was dissolved in a minimum amount of boiling toluene and placed in the freezer (–10 °C) to give colourless blocks of 3b-C\textsubscript{7}H\textsubscript{8} suitable for X-ray crystallography (m.p. 245–250 °C dec.) The NMR data showed that the crystals lost some of the toluene over time to reduce to a ratio of 0.4:1. The elemental analysis was performed during the same week as the NMR was performed; therefore, the elemental analysis data given are for the 0.4:1 ratio crystal. Found: C, 76.1; H, 3.4. X-ray Crystallography is the likely source for higher residuals in both the integration and final refinements for this structure; E-density map using the SQUEEZE routine of PLATON (details in the CIF file) [52].

3.3.5. Lithium Ketoiminate Complex 3c Solvate

Procedure as for 3b from 0.508 g (1.858 mmol) of 1c and 1.2 mL (1.92 mmol) of 1.6 M BuLi, heated to 80 °C to dissolve. The reaction was then allowed to cool to room temperature which resulted in the formation of white needle-like crystals (m.p. 124.8–131.8 °C, dec.) suitable for crystallography. These crystals do not dissolve in C\textsubscript{6}D\textsubscript{6} at 25 °C; in 1:1 C\textsubscript{6}D\textsubscript{6}/THF-d\textsubscript{8}, the same NMR spectrum is obtained as recorded for 2c. δ\textsuperscript{(\textit{H})} (C\textsubscript{6}D\textsubscript{6}, 25 °C): δ = 2.45 (br).

3.3.6. Lithium Ketoiminate Complex 3d

Procedure as for 2a from 0.706 g (3.05 mmol) 1d in 10 mL of THF and 2.0 mL (3.2 mmol) of 1.6 M BuLi in hexanes. After removal of THF in vacuum, the residue was dissolved on heating in 4 mL of heptane and 0.7 mL of dry THF placed in the freezer (–10 °C) to give in yellow crystals of 3d suitable for X-ray crystallographic study. m.p. 244–250 °C, dec. NMR: δ\textsuperscript{(\textit{H})} (C\textsubscript{6}D\textsubscript{6}, 25 °C) 6.86 (2H, s, \textit{meta} CH), (1H, s, backbone CH), 2.21 (3H, s, para CH\textsubscript{3}), 2.18 (6H, s, \textit{ortho} CH\textsubscript{3}), 1.92 (3H, s, backbone CH\textsubscript{3}), 1.61 (3H, s, backbone CH\textsubscript{3}), 1.56 (3H, s, backbone CH\textsubscript{3}). δ\textsuperscript{(\textit{C})} (C\textsubscript{6}D\textsubscript{6}, 25 °C): 172.69, 170.08, 147.83, 132.03, 129.24, 129.07, 127.51, 100.64, 27.36, 21.35, 20.83, 18.25, 17.85. δ\textsuperscript{(\textit{H})} (C\textsubscript{6}D\textsubscript{6}, 25 °C): +1.44.

3.4. X-ray Crystallography

Crystals of 1a–d, 2a–c and 3b–d were mounted on glass fibres in Paratone\textsuperscript{TM} oil and cooled to 173 K in a cold gas stream of the Bruker Kryoflex apparatus and reflection data were collected on an Apex II CCD area-detector diffractometer. Data collection was controlled by APEX2, cell refinement and data reduction was performed with SAINT-Plus and a multiscan absorption correction was applied in each case using SADABS [49]. The structures were solved with SHELXS97 and refined with SHELXTL [50]. Key crystal and refinement data are reported in Table A1 (Appendix B), while archival data are provided in the ESI as CIF files. H atoms were refined using a riding model with the exception of the N(1)–H atoms in 1a–d which were refined freely with isotropic temperature factors. The structure of 3b contains free toluene in the lattice that is disordered in a typical “head-to-tail” fashion [51] with refined occupation of 78:22 and retains a high degree of thermal motion even at 173 K. Solvent in the lattice of 3c was even more poorly defined and we ended up subtracting its contribution to the E-density map using the SQUEEZE routine of PLATON (details in the CIF file) [52]. This lattice solvent is the likely source for higher residuals in both the integration and final refinements for this structure;
the model for 3c itself seems to be robust despite these factors and the “conventional” R-factor (6.54%) is in the normal range. CCDC 1540147–1540156 contain the data deposition for the crystal structures. These data can be obtained, free of charge, via http://www.ccdc.cam.ac.uk/products/csd/request/ (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk)).

3.5. Computation

DFT calculations for the molecules were done using B3LYP with the 6-31G(d) basis set using Gaussian 03 and visualized with Gaussview 4.1.2 for Windows [53]. All the geometries could be minimized and frequency calculations verified that these are at least local minima for all cases, except for 4c, for which the geometry never fully converged. The minimized structures are included with the X-ray geometries in the archival CIF file available as ESI.

4. Conclusions

This work reports a detailed structural comparison for two types of ketoiminate complexes of lithium from crystal structures obtained during synthesis. From solutions strongly enriched in THF, transoid Li2O2 squares are generally obtained, with each lithium cation further coordinated by a THF solvent molecule. Changes in structures of the free ligands and the complexes are observed between the common 3,5-dimethylketamines and the more sterically bulky 3,4,5-trimethylketamines, with shorter cross-ring O···N distances in free and coordinated chelate rings. More curious was the observation that with ligand 1d, the cuboidal Li4O4 structure is formed in the presence of THF. Similar complexes could be obtained for 3b,d by excluding THF entirely and replacing it with only hydrocarbon solvents. The NMR evidence in either pure deuterated benzene or in benzene/THF mixtures fits for the desolvated cubane structures as the dominant solution species under these conditions. DFT calculations show that the gas-phase energetic preference is for the transoid square complexes; however, this does not take the solvation and especially the entropic preference for the desolvated cubanes into consideration. Whereas Dipp and Mes-substituents are generally regarded as quite similar, the structures of the cuboidal clusters show significant differences between clusters formed from the two classes of ligands. The unexpectedly low solubility of the Dipp derivatives seems to be correlated with a more uniform cluster geometry and a very smooth, unbroken, surface. These results, which contradict the normal solubility trends for Dipp- and Mes-derivatives, will be of interest to those wishing to use the lithium salts as reaction intermediates for ligand transfer to other metals: these lithium β-ketoiminates are likely to be considerably more reactive when produced and handled in donating solvents such as THF than if they are prepared for use in a non-polar and non-coordinating solvent. With regards to functional properties, it would appear that the external ligand “sheathing” effects can play significant roles and should not be ignored by an undue focus on just the common Li4O4 core structures.

Supplementary Materials: The following are available online at www.mdpi.com/2304-6740/5/2/30/s1, electronic file in CIF format with crystal coordinate data for 1a–d, 2a–c, 4b–d, and DFT optimized geometries from B3LYP/6-31G(d) calculations for 1a–d, 2a–d, 3a–d and 3c’, 3d’ computed with the alternative S4 geometry.

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Author Contributions: Twyla Gietz and René T. Boeré conceived and designed the experiments; Twyla Gietz performed the experiments; Twyla Gietz and René T. Boeré analyzed the data; and Twyla Gietz and René T. Boeré wrote the paper.

Conflicts of Interest: The authors declare no conflict of interest.
Appendix A

Figure A1. Depiction of the hydrogen-bonding that forms a centrosymmetric dimer in the structure of 1b. The dihedral angle between the $N_1-O_1-N_1'-O_1'$ and the $O_1-C_2-C_3-C_4-N_1$ planes is only $16.5^\circ$.

Figure A2. Space-filling depictions of the cuboidal Li$_4$O$_4$ ketoiminate clusters (a) 3b and (b) 3c, emphasizing the globular nature of the latter and the more angular and clefted nature of the former.

Figure A3. Orientation and distance of ketoiminate methyl carbon atoms (coloured orange) to aryl ring centroids (light green) of the adjacent ligands. Contrast the longer distances and poorer orientation in (a) 3b with the more favourable situation in (b) the structure with the refcode BAMFAX (see [7]).
### Table A1. Crystal data, structure collection and refinement data for X-ray crystallography

#### (A)

| Parameter | 1a         | 1b         | 1c         | 1d         |
|-----------|------------|------------|------------|------------|
| Formula   | C₁₇H₂₅NO  | C₁₄H₂₅NO  | C₁₆H₂₅NO  | C₁₁H₂₅NO  |
| FW, amu   | 259.38     | 217.30     | 273.41     | 231.33     |
| T, K      | 173(2)     | 173(2)     | 173(2)     | 173(2)     |
| λ, Å      | 0.71073    | 0.71073    | 0.71073    | 0.71073    |
| Crystal system | orthorhombic | monoclinic | orthorhombic | monoclinic |
| Space group | Pccn       | P₂₁/n     | P₂₁2₁2₁   | C₂/c       |
| Cell: a, Å | 12.3641(12)| 10.0068(6) | 6.7423(4)  | 18.8762(17) |
| b, Å      | 16.3858(16)| 9.8961(6)  | 13.9706(8) | 8.0097(7)  |
| c, Å      | 15.4945(15)| 12.7933(8) | 18.0631(10)| 19.0037(17)|
| α, °      | 90         | 90         | 90         | 90         |
| β, °      | 90         | 90         | 90         | 90         |
| γ, °      | 90         | 99.1380(10)| 90         | 107.5430(10)|
| V, Å³     | 3139.1(5)  | 1250.82(13)| 1701.44(17)| 2739.6(4)  |
| Z         | 8          | 4          | 4          | 8          |
| Dcalc, g/cm³ | 1.098     | 1.154     | 1.067     | 1.112     |
| µ, mm⁻¹   | 0.067      | 0.072      | 0.065      | 0.069      |
| F(000)    | 1136       | 472       | 600       | 1008      |
| Cryst. size, mm³ | 0.54 × 0.41 × 0.20 | 0.27 × 0.25 × 0.14 | 0.42 × 0.20 × 0.14 | 0.43 × 0.34 × 0.16 |
| θmin, max, ° | 2.06, 26.73 | 2.41, 27.10 | 1.84, 27.40 | 2.25, 27.48 |
| h/min, max | −15, 15   | −12, 12    | −8, 8     | −24, 24   |
| k/min, max | −20, 20   | −12, 12    | −18, 18   | −10, 10   |
| l/min, max | −19, 19   | −16, 16    | −23, 23   | −24, 24   |
| Rf_all    | 40165     | 17205     | 24505     | 19053     |
| Rf_indep, Rint | 3338, 0.0561 | 2762, 0.0254 | 2224, 0.0285 | 3153, 0.0240 |
| Compl., β, ° | 100, 26.73 | 99.9, 27.10 | 100, 25.25 | 99.9, 27.48 |
| Abs corr. | semi-empirical from equivalents |
| Max/min, e-Å⁻³ | 0.9868, 0.9646 | 0.9914, 0.9378 | 0.9916, 0.9279 | 0.9918, 0.9169 |
| Data      | 3338       | 2762       | 2224       | 3153       |
| Restraints | 0          | 0          | 0          | 0          |
| Parameters | 182        | 153        | 191        | 163        |
| GOF       | 1.032      | 1.047      | 1.031      | 1.053      |
| R₁ (I > 2σI) | 0.0428    | 0.0462     | 0.0407     | 0.0465     |
| wR₂ (all data) | 0.1201 | 0.1349     | 0.1172     | 0.1402     |
| Max, min, e-Å⁻³ | 0.20, −0.21 | 0.26, −0.31 | 0.20, −0.18 | 0.26, −0.22 |

#### (B)

| Parameter | 2a         | 2b         | 2c         |
|-----------|------------|------------|------------|
| Formula   | C₄₂H₄₄Li₂N₂O₄ | C₃₆H₃₂Li₂N₂O₄ | C₄₄H₄₆Li₂N₂O₄ |
| FW, amu   | 674.83     | 590.68     | 702.88     |
| T, K      | 173(2)     | 173(2)     | 173(2)     |
| λ, Å      | 0.71073    | 0.71073    | 0.71073    |
| Crystal system | triclinic | monoclinic | monoclinic |
| Space group | P T        | P₂₁/c     | P₂₁/n     |
| Cell: a, Å | 9.4060(8)  | 8.0148(5)  | 20.843(5)  |
| b, Å      | 10.7931(9) | 15.0628(9)| 10.495(2)  |
| c, Å      | 11.9959(10)| 14.5918(9)| 21.365(5)  |
| α, °      | 69.0400(10)| 90         | 90         |
| β, °      | 73.6160(10)| 103.8550(10)| 112.886(2) |
| γ, °      | 67.0160(10)| 90         | 90         |
| V, Å³     | 1032.50(15)| 1710.35(18)| 4305.7(17) |
| Z         | 1          | 2          | 4          |
| Dcalc, g/cm³ | 1.085     | 1.147     | 1.084     |
| µ, mm⁻¹   | 0.067      | 0.073      | 0.067      |
| F(000)    | 368        | 640        | 1536       |
### Table A1. Cont.

#### (B)

| Parameter                | 2a                              | 2b                              | 2c                              |
|--------------------------|---------------------------------|---------------------------------|---------------------------------|
| Cryst. size, mm$^3$      | $0.36 \times 0.20 \times 0.12$ | $0.39 \times 0.18 \times 0.11$ | $0.46 \times 0.19 \times 0.17$ |
| $\theta_{\text{min, max}}$, $^\circ$ | 1.84, 26.03                     | 1.97, 27.48                     | 1.75, 27.48                     |
| $h$ min, max             | $-11, 11$                       | $-10, 10$                       | $-27, 27$                       |
| $k$ min, max             | $-13, 13$                       | $-19, 19$                       | $-13, 13$                       |
| $l$ min, max             | $-14, 14$                       | $-18, 18$                       | $-27, 27$                       |
| R(B) all                 | 10854                           | 19537                           | 60577                           |
| R(f) indep, R(int)       | 4040, 0.0245                    | 3919, 0.0373                    | 9865, 0.0250                    |
| Compl. $\% \theta$, $^\circ$ | 99.6, 25.25                     | 100.0, 25.25                    | 99.9, 27.48                     |
| Abs corr.                | semi-empirical from equivalents |                                 |                                 |
| Max/min trans.           | 0.9918, 0.9136                  | 0.9916, 0.8956                  | 0.9918, 0.9266                  |
| Data                     | 4040                            | 3919                            | 9865                            |
| Restraints               | 0                               | 0                               | 0                               |
| Parameters               | 232                             | 204                             | 483                             |
| GOF                      | 1.035                           | 1.025                           | 1.030                           |
| $R_1$ ($I > 2\sigma(I)$ | 0.0464                          | 0.0495                          | 0.0453                          |
| $wR_2$ (all data)        | 0.1274                          | 0.1409                          | 0.1285                          |
| Max, min, e·Å$^{-3}$     | $0.23, -0.19$                   | $0.24, -0.25$                   | $0.32, -0.21$                   |

#### (C)

| Parameter                | 3b                              | 3c                              | 3d                              |
|--------------------------|---------------------------------|---------------------------------|---------------------------------|
| Formula                  | $C_{56}H_{72}Li_4N_4O_4\cdot C_7H_8$ | $C_{72}H_{104}Li_4N_4O_4$       | $C_{60}H_{80}Li_4N_4O_4$        |
| FW, amu                  | 985.07                          | 1117.35                         | 949.04                          |
| $T$, K                   | 173(2)                          | 173(2)                          | 173(2)                          |
| $\lambda$, Å             | 0.71073                         | 0.71073                         | 0.71073                         |
| Crystal system           | orthorhombic                    | monoclinic                      | monoclinic                      |
| Space group              | $P2_12_12_1$                    | $P2_1/n$                        | $P2_1/n$                        |
| Cell: $a$, Å             | 13.7530(9)                      | 14.3398(14)                     | 17.0567(11)                     |
| $b$, Å                   | 18.3062(13)                     | 27.5043(3)                      | 26.6472(2)                      |
| $c$, Å                   | 24.0940(17)                     | 19.8735(19)                     | 16.4969(14)                     |
| $\alpha$, $^\circ$       | 90                              | 90                              | 90                              |
| $\beta$, $^\circ$        | 90                              | 107.4870(10)                    | 91.2180(10)                     |
| $\gamma$, $^\circ$       | 90                              | 90                              | 90                              |
| $V$, Å$^3$               | 6065.1(7)                       | 7475.9(13)                      | 5737.1(8)                       |
| $Z$                      | 4                               | 4                               | 4                               |
| $D_{\text{calc}}$, g/cm$^3$ | 1.079                          | 0.993                           | 1.099                           |
| $\mu$, mm$^{-1}$         | 0.065                           | 0.059                           | 0.067                           |
| $F(000)$                 | 2120                            | 2432                            | 2048                            |
| Cryst. size, mm$^3$      | $0.48 \times 0.40 \times 0.24$ | $0.69 \times 0.27 \times 0.13$ | $0.40 \times 0.22 \times 0.22$ |
| $\theta_{\text{min, max}}$, $^\circ$ | 1.69, 27.48                     | 1.66, 25.03                     | 1.75, 27.48                     |
| $h$ min, max             | $-17, 17$                       | $-17, 17$                       | $-16, 16$                       |
| $k$ min, max             | $-23, 23$                       | $-32, 32$                       | $-34, 34$                       |
| $l$ min, max             | $-31, 31$                       | $-23, 23$                       | $-21, 21$                       |
| Measured rfl             | 70155                           | 88683                           | 82309                           |
| Indep. rfl, R$\text{int}$ | 7604, 0.0372                    | 13200, 0.0921                   | 13161, 0.0572                   |
| Compl. $\% \theta$, $^\circ$ | 100.0, 25.25                    | 100.0, 25.03                    | 100.0, 27.48                    |
| Abs corr.                | semi-empirical from equivalents |                                 |                                 |
| Max/min trans.           | 0.9842, 0.9692                  | 0.9918, 0.8738                  | 0.9843, 0.9016                  |
| Data                     | 7604                            | 13200                           | 13161                           |
| Restraints               | 84                              | 0                               | 0                               |
| Parameters               | 762                             | 785                             | 673                             |
| GOF                      | 1.039                           | 0.985                           | 1.011                           |
| $R_1$ ($I > 2\sigma(I)$ | 0.0386                          | 0.0654                          | 0.0532                          |
| $wR_2$ (all data)        | 0.1077                          | 0.1786                          | 0.1478                          |
| Max, min, e·Å$^{-3}$     | $0.21, -0.16$                   | $0.25, -0.19$                   | $0.26, -0.19$                   |

1 See deposited CIF files for full data.
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