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Towards Hexagonal Planar Nickel: A Dispersion-Stabilised Tri-Lithium Nickelate

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Abstract: Advancing the understanding of lithum nickelate complexes, here we report a family of homoleptic organonickelate complexes obtained by reacting Ni(COD)₂ and lithium aryl-acetylides in the presence of the bidentate donor TMEDA. These compounds represent rare examples of low-valent transition-metals supported solely by organolithium ligands. Whilst the solid-state structures indicate a hexagonal planar geometry around Ni(0) with Ni-Li bonds, bonding analysis via QTAIM, NCI, NBO and ELI methods reveals that the Ni-Li interactions are repulsive in nature, characterising these complexes as tri-coordinated. London dispersion forces between TMEDA and the organic substituents on nickel are found to play a crucial role in the stabilisation and thus isolation of these complexes. Preliminary reactivity studies demonstrate that the homoleptic lithium nickelates undergo stoichiometric cross-coupling with PhI to give dinickel clusters containing both anionic acetylide and neutral alkyne ligands.

Six-coordinate transition-metals adopting a hexagonal planar geometry, whilst known for polynuclear clusters,^{1–3} condensed phases^{4–6} or within the pores of coordination polymers,⁷ are remarkably rare for discrete transition-metal complexes. Well-defined hexagonal planar palladium complexes were reported by Crimmin and co-workers in 2019,⁸ and this has recently been extended to the platinum congener (I, Scheme 1a).⁹ Prior to these studies, hexagonal planar nickel complexes such as [Ni(P⁴Bu)₆] were reported,¹⁰ however subsequent theoretical studies revealed that these and related species are best described as trigonal planar complexes with a 16 electron count,¹¹ akin to classical Ni(0) *tris*-olefin compounds.^{12,13} The bonding scenario in I is markedly different, however, as it combines an alternating array of σ -donating (H⁻) and σ -accepting (LMg⁺) ligands, in which the M···Mg interactions are primarily ionic in nature.^{8,9}

The overlooked tri-lithium nickelate "Li₃NiPh₃(solv)₃" (**II**, Scheme 1b), which possesses similar structural features to **I**, was documented by Taube in 1979.^{14,15} Recently, however, we have reported that this proposed structure was misassigned and instead identified as an octanuclear cluster containing a bridging C₆H₄ ligand between two nickel centres, **III**.¹⁶ Although Fe(0) complexes supported solely by phenyl-lithium ligands are known,¹⁷ the isolation of **III** suggests that this is not possible for d^{10} Ni(0), leading to the *in situ* formation of the π -accepting, and formally reduced, C₆H₄ ligand in order to alleviate the extreme electron density at nickel. This hypothesis is further supported by the isolation of related side-on N₂ complexes obtained when treating Ni(CDT) (CDT = 1,5,9-cyclododecatriene) with an excess of PhLi or PhNa under an N₂ atmosphere.^{18–20} Based on these findings, we reasoned that a carbanionic ligand which itself could serve as a suitable π -acceptor would facilitate the synthesis and isolation of a hexagonal planar nickel complex (**IV**, Scheme 1c).



Scheme 1. Examples of hexagonal planar transition-metal complexes.

Treatment of Ni(COD)₂ (COD = 1,5-cyclooctadiene) with 3 equivalents of lithium phenyl-acetylide **1a** in the presence of a slight excess of bidentate donor TMEDA (TMEDA = N, N, N', N'tetramethylethylenediamine) afforded a deep purple reaction mixture which deposited the target complex Li₃(TMEDA)₃Ni(C=C-Ph)₃ **2a** as a bronze microcrystalline solid in 81% yield after filtration and washing (Figure 1a). This could be extended to other lithium aryl-acetylides to give **2b** (Ar = p-Tol) and **2c** (Ar = 3-thienyl) in 85% and 28% yield, respectively (see SI

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Figure 1. a) Synthesis of tri-lithium nickelates 2a-c; b) Synthesis of lithiumnickelate cluster 3; c) Molecular structure of 2a shown with thermal ellipsoids at 30% probability. Hydrogen atoms and co-crystallised solvents omitted for clarity. Selected bond lengths (Å): Ni1–C9 1.856(2); Ni1–C1 1.8683(18); C9–C10 1.233(4); C1–C1 1.232(3); Ni1–Li1 2.512(3); Ni1–Li2 2.487(4); Li1–C9 2.264(4); Li1–C1 2.268(4); Li2–C1 2.228(4).

for details and solid-state structures). Akin to other alkali-metal nickelates that we have reported, the choice of solvent and donor is key to enabling their synthesis and isolation.16,21,22 Et₂O and THF solvates of 2a could not be isolated or spectroscopically observed, and the addition of 12-crown-4 to 2a leads to immediate decomposition, illustrating that TMEDA plays an important role beyond lithium cation solvation (vide infra). Demonstrating the importance of the choice of alkynyl ligand, when using more electron-rich lithium acetylides such as Me₃Si-C=C-Li (1d) the polynuclear cluster [Li6(TMEDA)3.5Ni2(C=C-SiMe3)6]2 (3) was formed (Figure 1b). This complex bears structural similarities to III in which a terminal lithium acetylide coordinates side-on between two nickel centres (see SI for experimental details and solid-state structure). Compounds 2a-c are diamagnetic and show wellresolved ¹H, ⁷Li and ¹³C NMR spectra with signals in the expected range: for 2a the acetylide signals are observed in the ¹³C NMR spectrum at δ 144.1 and 100.7 ppm, respectively.²³

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The solid-state structure of 2a (Figure 1c) shows an apparent six-coordinate, perfectly planar environment around Ni in which the TMEDA solvated lithium cations occupy sites nestled between the Ni-acetylides. The phenyl-substituents and TMEDA donors are orientated perpendicular to the planar core. The C-Ni-Li angles occupy a narrow range from 59.53(5)° to 60.25(10)°, consistent with a hexagonal planar geometry.9 The Ni-C distances [Ni1-C1 1.8683(18) Å; Ni1-C9 1.856(2) Å] and C≡C bond lengths [C1-C2 1.232(3) Å; C9-C10 1.233(4) Å] are comparable to reported low-valent nickel acetylides,24 whilst the Li-C contacts [2.228(4)-2.267(4) Å] are typical for metalates containing TMEDA-solvated lithium acetylides.25,26 The Ni-Li distances range from 2.487(4) Å to 2.512(3) Å which is within the sum of the covalent radii (2.52 Å)27 and comparable to other lithium organonickelates derived from PhLi that we have reported containing TMEDA.²² A Hirshfeld surface analysis²⁸ of 2a (Figure 2a), in which red regions depict where contact distances between closest atoms below and above the surface are smaller than the sum of their van der Waals radii, further illustrates the existence of close contacts between Ni-Li and Li-C. In addition, there are red regions for close contacts significantly below the sum of atomic C and H van der Waals radii between the TMEDA methyl groups and the phenyl-acetylide substituents on nickel.

Since geometrical proximity is not necessarily an indicator of a bonding interaction, we further assessed the nature of the Ni-Li, Li-C and TMEDA-acetylide interactions and the overall bonding in 2a by a complementary bonding analysis.²⁹ Isolated molecule geometry optimisations of the entire complex 2a were conducted at the B3LYP/def2-TZVP level including empirical GD3BJ dispersion corrections.³⁰ A subsequent Quantum Theory of Atoms in Molecules (QTAIM)31 topological analysis of the quantum-mechanical electron density yielded bond paths and corresponding bond critical points (bcps) for all Ni-C and Li-C interactions, but none for the Ni-Li contacts (Figure 2b). According to Bader, bond paths can be understood as bonding interactions - and the absence of bond paths as the absence of bonding interactions.³² Hence, QTAIM presents the first indication of only a tri-coordinated nickel center despite the apparent Li proximity. The non-covalent interaction (NCI)33 index clarifies the nature of the interactions as repulsive (red color), attractive (blue color) and weakly attractive (green-brown) (Figure 2c). It is striking that the forces prevailing along the Ni-Li axes are clearly repulsive, indicating that nickel is certainly not coordinated or bonded to lithium. Instead, in agreement with the bond paths motif, there are attractive interactions between the Li atoms and the C atoms of the acetylide substituents. These features contrast significantly to the hexagonal planar complexes reported by Crimmin (see I, Scheme 1a), which show QTAIM bond paths and attractive interactions (NCI plot) between the transition-metal (Pd, Pt) and s-block metal (Mg).^{8,9}

Figures 2b and 2c also shed light on the interactions between the methyl groups of the TMEDA donor and the acetylide and phenyl carbon atoms of the C=C–Ph ligands. Figure 2b shows various H···C bond paths in the electron density topology, whilst many broad NCI surfaces colored green between these groups are observed in Figure 2c. These represent attractive London dispersion (van der Waals) interactions,³⁴ and, although weak in nature, summed up over large areas of space they can significantly stabilise compounds to facilitate their isolation. In this optimised geometry, the sum of all Grimme-type terms between

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Figure 2. a) Hirshfeld surface analysis of **2a** with the property d_{norm} colour-coded onto it: Red = contact distance between closest atom below and above the surface smaller than the sum of their van der Waals radii (Σ vdW); white = contact distance equal to Σ vdW; blue = contact distance larger than Σ vdW. b) Electron density contour map with the molecular graph according to QTAIM. Solid bond paths mean that there is high electron density at the corresponding bcps (orange balls); dashed means low electron density at the bcps. c) Isosurface representation of the reduced density gradient s (NCI index) at s(r) = 0.5 color coded with sign(λ_2)p: Red = repulsive; blue = attractive; green = weakly attractive.

C=C–Ph and TMEDA ligands amounts to 77.5 kJ mol⁻¹. If compared to the geometry obtained upon optimisation without GD3BJ empirical dispersion correction, this geometry is energetically more favorable by 754 kJ mol⁻¹ mostly owing to some rearrangements in the TMEDA methyl groups. This striking importance of London dispersion between the ligands is supported experimentally by unsuccessful attempts to isolate or spectroscopically observe similar complexes with different Li cation donors such as Et₂O, THF or 12-crown-4 (*vide supra*). Hence, complexes **2a–c** are further examples in a row of recently discovered dispersion-stabilised molecules.^{34–37}

The atomic NPA/QTAIM charges [NPA = natural population analysis, in the framework of natural bond orbital (NBO) analysis]³⁸ for the Ni atom in **2a** are 0.33/0.30e. The terminalacetylide carbon atoms are negatively charged with -0.56/-0.41e, with the remaining negative charges delocalised over the rest of the C=C-Ph ligands. This shows that the overall direction of charge transfer is from the Ni atom towards the ligands, and that the Ni atom can be only formally described as a neutral Ni(0) center. The Li atoms are attracted electrostatically to the electron rich terminal C atoms of the acetylide groups (Figure 2c, blue extensions of the NCI surfaces attached to the red regions depicting Ni-Li repulsion), but in addition the reduced positive charge of the Li atoms (0.82/0.87e, NPA/QTAIM) indicates some minor orbital overlap with the C=C π -system, which explains the occurrence of the Li···C bond paths in Figure 2b.

Significant back-bonding between the Ni atom and the acetylide unit is the mechanism behind the Ni \rightarrow C charge transfer discussed in the previous paragraph. It can be depicted as a d-orbital (d_{xy} and d_{x2-y2}) to $\pi^*_{(C\equiv C)}$ interaction in NBO, as visualised in Figure 3a. Each of these Ni \rightarrow C=C–Ph back-bonding interactions (3 times) amounts to 48 kJ mol⁻¹, which is approximately a sixth of the energy of the forward σ -bonding interaction.³⁹ Back-bonding from the out-of-plane Ni d-orbitals (d_{xz} and d_{yz}) to the orthogonal $\pi^*_{(C\equiv C)}$ anti-bonding orbital is also observed, together with a weak back-bonding interaction from the Ni d_{z2} to $\sigma^*_{(C\equiv C)}$ orbital (see Figures S26–28). These non-Lewis backbonding perturbations stabilises the complex, but weakens

the C≡C bond considerably; the bond orders are 2.36 (delocalisation index, DI)⁴⁰ or 2.56 (NLMO/NPA bond order; NLMO = natural localized molecular orbital, within NBO theory) instead of the expected 3.0. The loss in electrons of the C≡C bond can also be quantified using the Electron Localizability Indicator (ELI).⁴¹ It indicates that there are only 4.6 instead of 6.0 electrons inside the bond basin of the formal triple bond (Figure 3b). The Ni-C bond orders are, in turn, 1.0 in both DI and NLMO/NPA schemes. The electron distribution in the Ni-C interaction is more complex, though, because due to the back-bonding the entire 4s/3d-shell of the Ni atom has merged with the carbon lone pairs. This is visualised in Figure 3b by localisation domains representing disynaptic V₂(Ni,C) ELI basins which are populated with 5.2e each (3 times). Note that the localisation domains are isosurface representations that only show the region around the source of the basin (the basins themselves are space-filling). This means that here the highest localisation of valence electrons is close to the C atoms and distant to the Ni atom. It is also noteworthy that the core shell of the Ni atom (3s, 3p electrons) is polarised in the ligand field, reflecting its symmetry. Ligand induced charge localisations⁴² alternate with depletions, and the latter point towards the highly populated C-Ni bond basins. Full details regarding the computations, software used and bonding analyses are given in the supporting information.

Thus, while based on the structural analysis it can be tempting to describe lithium nickelates **2a–c** as hexagonal planar organonickel complexes, careful analysis of the bonding present in these systems indicates that they are best described as trigonal planar species.

Having investigated the structure and bonding of the homoleptic tri-lithium nickelates, the reactivity of **2a** was explored. No reaction was observed with phosphines (PCy₃ or PEt₃) reflecting the quenched Lewis acidity at the nickel center. This is in stark contrast to the non-isolable nickel analogue of **I** (see Scheme 1a) which coordinates PCy₃ in the axial position to give a 7-coordinate hexagonal pyramidal complex.⁸ However, compound **2a** reacts cleanly with one equivalent of iodobenzene to give hexanuclear cluster **4a** alongside diphenylacetylene and

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Lil (Figure 4a). Complex **4a** forms in 80% spectroscopic yield from **2a** (see Figure S10) or can be independently prepared directly from Ni(COD)₂, Ph–C=C–Li and Ph–C=C–Ph (1:2:0.5 ratio) as the Et₂O solvate in 49% crystalline yield. No further reaction is observed on the addition of excess iodobenzene, and complex **2a** cannot be regenerated by treatment of **4a** with Ph–C=C–Li, rendering this system incapable of catalytic Sonogashira-type cross-coupling.⁴³



Figure 3. a) Visualisation of the overlap of the natural bond orbitals representing a Ni d-orbital and a C=C antibonding π orbital. This non-Lewis contribution to bonding contributes a stabilisation energy (E2 energy) of 48 kJ mol⁻¹. b) ELI localisation domain representation at an isovalue of 1.40. The domains represent basins in ELI, disynaptic ones are labelled as V₂, and the total electron population of each Ni–C and C–C basin is given (they occur three times each).

The solid-state structure of **4a**.Et₂O (Figure 4b) adopts a distorted Li₄N₂ core in which diphenylacetylene coordinates sideon between two *pseudo*-trigonal planar nickel centres. This motif is reminiscent of that observed in the μ - η^2 - η^2 -C₆H₄ complex (III, see Scheme 1b)¹⁶ and related N₂ complexes.^{18–20} Elongation of the C2–C3 bond [1.371(2) Å; *cf.* 1.198(2) Å for Ph–C≡C–Ph]⁴⁴ and bending away from linearity [C1–C2–C3 = 134.0(1)°] indicates significant back-donation from the electron-rich Ni centres, as previously observed for III (see Scheme 1b).¹⁶ The C–Ni–C angles in **4a** are considerably narrower compared to **2a** [104.32(6)° for C23–Ni1–C15 in **4a** vs. 120.47(5)° for C9–Ni1–C1 in **2a**]. This leads to longer Ni…Li distances [range = 2.608(2) Å to 2.668(2) Å] which are outside the sum of the covalent radii (2.52 Å),²⁷ and contracted Li…C distances [range = 2.080(3) Å to 2.485(3) Å] including interactions with both carbon atoms of the acetylide π -system, a feature not observed in compounds **2a–c**.



Figure 4. a) Synthesis of lithium nickelate 4a; b) Molecular structure of 4a.Et₂O shown with thermal ellipsoids at 30% probability.⁴⁵ Hydrogen atoms omitted and ethyl groups of coordinated Et₂O shown as wireframe for clarity. Selected bond lengths (Å) and angles (°): C2–C3 1.371(2); Ni1–C2 1.937(1); Ni1–C3 1.972(1); Ni1–Ni2 2.6713(5); Ni1–C15 1.891(2); Ni1–C23 1.896(1); C2–Ni1–C3 41.05(5); C15–Ni1–C23 104.32(6).

In conclusion, we have demonstrated that homoleptic trilithium nickelates can be readily accessed from Ni(COD)₂ and lithium aryl-acetylides in the presence of TMEDA. Whilst interpretation of the bond distances and angles implies a hexagonal planar geometry, complementary bonding analysis reveals that the Ni…Li interactions are repulsive, characterising these compounds as trigonal planar. Dispersion interactions between the Li-TMEDA units and the aryl-acetylide substituents were found to stabilise the compounds and thus facilitate their isolation. These results shed new light on the structure and bonding of heterobimetallic nickelate complexes, and show that for unusual compounds, geometrical analysis can be misleading and bonding analysis is crucial.

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Keywords: nickel • organolithium • transition-metal complexes • complementary bonding analysis • London dispersion

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- [45] Deposition Numbers 2180282 (for 2a), 2180283 (for 2b), 2180284 (for 2c), 2180285 (for 3), 2180286 (for 4a), 2083516 (for 4a) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

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Homoleptic tri-lithium nickelates can be readily prepared from simple precursors, but despite exhibiting a hexagonal planar geometry according to solid state parameters, complementary bonding analysis reveals that the Li–Ni interactions are repulsive in nature. London dispersion interactions between the TMEDA donor and aryl-acetylide ligands are found to be crucial in the stabilisation and isolation of these complexes.

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