

A double salt with remarkable supramolecular channels: Synthesis and crystal structure of bis[1,3-dimesitylimidazolium] tetrachloronickelate(II)–[1,3-dimesitylimidazolium]chloride, which contains substituted imidazolium cations, and both tetrachloronickelate(II) and chloride anions



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ABSTRACT

The reaction of nickel(II) acetylacetonate trimer with 1,3-bis(2,4,6-trimethylphenyl)imidazolium chloride, [IMesH]Cl, leads to the formation of the remarkable double salt [IMesH]₂[NiCl₄].[IMesH]Cl **2**, (or alternatively [IMesH]₃[NiCl₄]Cl). The solid-state structure of this species was determined by a single X-ray diffraction study. The molecular parameters of the ions are unremarkable, but this double salt crystallizes in the chiral space group *P*6₃ despite the achiral nature of all the ions: the chirality arises from the helical arrangement of the imidazolium mesityl groups. Additionally, the crystal contains hydrophobic channels of ca. 4.5 Å diameter, and there are extensive H-bonding interactions in the crystal. The double salt reacts with potassium *tert*-butoxide to give the known *bis*-*N*-heterocyclic carbene complex *trans*-[Ni(IMes)₂Cl₂], **3**.

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1. Introduction

Ionic compounds with imidazolium salts as cations and tetrahedral tetrachlorometallate anions have been intensively studied in recent years, as many such compounds often exhibit interesting physical and catalytic behavior [1].

Various imidazolium salts with tetrachloronickelate, as well as with other first row transition metal tetrachlorometallates as the counter ion, have been prepared and are of interest. Certain [NiCl₄]²⁻ salts with imidazolium [2] or alkylammonium [3] cations, exhibit thermochromic behavior, while others are ionic liquids at ambient temperature [4,5]. Such salts, frequently dispersed on silica, have been studied for various catalytic reactions, including the oxidation of styrene with H₂O₂ [6], Suzuki cross-coupling [7,8], Kharasch additions [6], hydroxymethylation reactions [9], and others. Studies of the electronic state of the nickel ion itself in such ionic liquid media have also been reported [10]. Previous synthetic methods for accessing imidazolium tetrachloronickelate salts

involved the direct thermal reaction of hydrated or anhydrous nickel(II) chloride with alkyl-substituted imidazolium salts, followed by, if necessary, removal of water under vacuum.

The chemistry of half-sandwich nickel(II) *N*-heterocyclic carbene (NHC) complexes of general formula [Ni(NHC)X(η⁵-C₅R₅)] (X = Cl, I; R = H, Me) has been under investigation by our group for several years now [11]. They are indeed inexpensive, readily synthesized *via* the direct reaction of nickelocene with imidazolium halide salts, [12] and highly reactive catalysts for a variety of organic reactions including Suzuki–Miyaura coupling [13], the hydrosilylation of aldehydes, ketones, and imines [14], and the α -arylation of ketones [15]. Recently we started to explore the chemistry of cyclopentadienyl-free nickel NHC complexes. These square planar compounds, of general formula [Ni(NHC)(acac)R] (acac = acetylacetonate), were readily prepared *via* displacement under acidic conditions of the η⁵-cyclopentadienyl ligand of cyclic and acyclic alkyl, NHC-nickel complexes, and subsequent treatment with potassium acetylacetonate (Scheme 1) [16]. Attempts to carry out the same methodology on the neutral complex, [Ni(IMes)ClCp] [12a], and on its cationic derivative, [Ni(IMes)(NCMe)Cp](PF₆) [13a], however always failed [16]. These negative results led us to

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investigate a more straightforward route to synthesize such compounds (*i.e.*, without going through a Cp removal step), and herein we describe the serendipitous synthesis of a tris(diarylimidazolium) tetrachloronickelate/chloride salt, [IMesH]₃[NiCl₄]Cl (**2**), from the reaction of anhydrous nickel(II) acetylacetonate with 1,3-bis(2,4,6-trimethylphenyl)imidazolium chloride, [IMesH]Cl **1**. The structure of this double salt shows a remarkable helical arrangement of the imidazolium units and of their associated mesityl rings, as well as microporous cylindrical channels of *ca.* 4.5 Å diameter, with the whole supramolecular assembly being held by strong hydrogen bonds.

2. Experimental

2.1. General comments

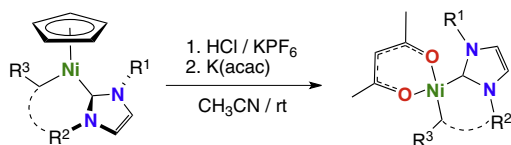
All reactions were carried out using standard Schlenk techniques under an atmosphere of dry argon. Solvents were distilled from appropriate drying agents under argon. Solution NMR spectra were recorded at 298 K on a FT-Bruker Ultra Shield 300 spectrometer operating at 300.13 MHz for ¹H, and at 75.47 MHz for ¹³C{¹H}. The chemical shifts are referenced to the residual deuterated or ¹³C solvent peaks. Chemical shifts (δ) and coupling constants (*J*) are expressed in ppm and Hz respectively. Commercial compounds were used as received. [Ni(IMes)₂Cl₂] was characterized by comparison of its ¹H and ¹³C{¹H} NMR spectra with the literature data [17]. The imidazolium salt [IMesH]Cl **1** was prepared according to the published method [18].

2.2. Synthesis of [IMesH]₃[NiCl₄]Cl (**2**)

A light-green suspension of anhydrous Ni(acac)₂ (154 mg, 0.599 mmol) and the imidazolium salt [IMesH]Cl **1** (613 mg, 1.797 mmol) in toluene (20 mL) was stirred at 110 °C for 48 h. A blue solid slowly formed. Removal of the remaining green suspension by syringe allowed the collection of the solid, which was then washed with toluene (3 × 5 mL) and *n*-pentane (3 × 5 mL), and dried *in vacuo* to afford **2** as a blue solid (145 mg, 0.126 mmol, 21%). ¹H NMR (CD₂Cl₂, 300.13 MHz): δ 7.82 (s, 2H, NCH), 7.23 (s, 4H, *m*-H), 6.86 (s, 1H, NCHN), 2.52 (s, 6H, *p*-Me), 2.23 (s, 12H, *o*-Me). ¹³C{¹H} NMR (CD₂Cl₂, 75.47 MHz): δ 141.7 (C_{Ar}), 139.0 (NCN), 134.7 (C_{Ar}), 131.1 (C_{Ar}), 130.6 (C_{Ar}), 123.9 (NCH), 23.6 (*o*-Me), 21.5 (*p*-Me).

2.3. Synthesis of *trans*-[Ni(IMes)₂Cl₂] (**3**)

A suspension of **2** (50 mg, 0.043 mmol) and KO^tBu (11 mg, 0.095 mmol) in toluene (10 mL) was stirred at room temperature for 24 h, during which the color slowly changed from blue to pale-orange. The reaction mixture was then filtered over Celite, and washed with toluene until the washings were colorless. Evaporation of the solvents afforded *trans*-[Ni(IMes)₂Cl₂] **3** as an orange solid (20 mg, 0.028 mmol, 64%).



Scheme 1. Synthesis of square planar [Ni(NHC)R(acac)] complexes via Cp acidolysis.

2.4. Crystallographic studies

Single crystals of [IMesH]₃[NiCl₄]Cl **2** suitable for a single-crystal X-ray analysis were grown by diffusion of *n*-pentane into a concentrated acetone solution of **2**. The crystals were covered with polyfluoroether oil and a single crystal was mounted on a nylon loop. The data were collected using graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å) on a Bruker AXS-KAPPA APEX II diffractometer equipped with an Oxford Cryosystem open-flow nitrogen cryostat. Cell parameters were retrieved using Bruker SMART software and refined using Bruker SAINT on all observed reflections. Absorption corrections were applied using SADABS [19]. The structure was solved and refined using direct methods with SIR2004 [20] and/or SHELXS-97 [21]. All programs are included in the package of programs WINGX-Version 1.80.01 [22] SHELXL [23]. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were inserted in idealized positions and allowed to refine riding on the parent carbon atom. Molecular diagrams were drawn with CrystalMaker 2 (version 8.7) or with Mercury 3.3. Data collection and structure refinement parameters, and crystallographic data are collected in Table 1.

3. Results and discussion

3.1. Serendipitous synthesis of [IMesH]₃[NiCl₄]Cl (**2**)

Direct reaction of commercially available Pd(acac)₂ with an excess of [IPrH]Cl in refluxing 1,4-dioxane for 24 h was reported to give [Pd(IPr)(acac)Cl] in very high yield [24]. However, reaction of Ni(acac)₂, which is trimeric and contains octahedrally coordinated nickel centers [25], with [IMesH]Cl (**1**) in refluxing toluene for 24 h did not afford the target complex, [Ni(IMes)(acac)Cl], but a large quantity of unreacted material, together with minor quantities ($\approx 10\%$) of a blue solid, **2** [26]. This species exhibited a ¹H NMR spectrum that corresponded in number and integrated intensities, to the free salt **1**; no resonances that could be attributed to acetylacetonate ligands were observed. However the chemical shifts were notably different from samples of pure **1** in the same solvent. The nature of this species being unclear, an X-ray diffraction study was carried out on a single crystal of **2** (*vide infra*). This revealed

Table 1
Crystal data and refinement details of compound **2**.

Compound	2
Molecular formula	C ₆₃ H ₇₅ Cl ₅ N ₆ Ni
Formula weight	1152.25
Crystal system	hexagonal
<i>T</i> (K)	150(2)
Crystal size (mm)	0.55 × 0.15 × 0.15
Crystal form, color	blue prism
Space group	<i>P</i> 6 ₃
<i>a</i> (Å)	15.9750(10)
<i>b</i> (Å)	15.9750(10)
<i>c</i> (Å)	15.4500(10)
α (°)	90
β (°)	90
γ (°)	120
<i>V</i> (Å ³)	3414.6(4)
<i>Z</i>	2
<i>D</i> _{calc} (g cm ⁻³)	1.121
μ (mm ⁻¹)	0.518
Reflections collected	17 373
Unique reflections, <i>R</i> _{int}	4021, 0.0656
No. of data with <i>I</i> > 2 σ (<i>I</i>)	2533
<i>R</i> ₁ , <i>wR</i> ₂ with <i>I</i> > 2 σ (<i>I</i>)	0.0515, 0.1143
Goodness-of-fit (GOF) on <i>F</i> ²	0.930

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