

# The Synthesis and Structure of Scandium Dichloride of Sterically Demanding Aminopyridinato Ligands

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**Abstract:** The reaction of the potassium salt of (2,6-diisopropylphenyl)-[6-(2,4,6-triisopropylphenyl)-pyridine-2-yl]-amine (Ap\*H) with the equimolar ratio of [ScCl<sub>3</sub>] in tetrahydrofuran (thf) resulted in the mononuclear mono(aminopyridinato) scandium dichloride complex [Ap\*ScCl<sub>2</sub>(thf)<sub>2</sub>]. An X-ray analysis showed the title compound to be monomeric. The compound [C<sub>40</sub>H<sub>59</sub>Cl<sub>2</sub>N<sub>2</sub>O<sub>2</sub>Sc] crystallized in the monoclinic space group, *P*2<sub>1</sub>/*n*, and possessed the following cell parameters: *a* = 12.4441(8) *b* = 22.9975(10) *c* = 13.9971(8) Å, β = 92.297(5)°, *V* = 4002.5(4) Å<sup>3</sup>, and *Z* = 4. Hirshfeld analyses show that H...H (91.1%), H...C/C...H (5.0%), and H...Cl/Cl...H (3.9%) are the contributing interactions in the solid-state structure. The compound was further characterized by NMR spectroscopy, and its purity was confirmed by elemental analysis.

**Keywords:** aminopyridine; aminopyridinate; N-ligand; scandium; single crystal; X-ray analysis

## 1. Introduction

Easy syntheses and the possibility of steric and electronic modification have made the coordination chemistry of 2-aminopyridines a very popular area of research [1,2]. The sterically very bulky variants introduced in 2004 have been proven to control the long-sought metal-to-ligand stoichiometry. These ligands carry substituted phenyl groups at the amine N-atom and the sixth position of the pyridine ring [3]. This has enabled the isolation of a large number of metal complexes across the periodic table not only in varying oxidation states but also with different coordination modes, such as chelating (common), bridging, or η<sup>1</sup>-binding (monodentate) fashion [2,4]. The ligand class has been used to stabilize transition metals in a very low oxidation state, leading to the isolation of quintuple-bonded complexes [5–7]. Their metal complexes have been used as catalysts for a range of applications [2,8,9]. These ligands are equally popular in amido lanthanoid chemistry. Slight variation in steric bulk has made the isolation of mono-, bis-, tris- and even tetrakis(aminopyridinate) lanthanoid complexes possible [10–13]. The formation of rare earth metals species of the [LnApX<sub>2</sub>(THF)<sub>n</sub>] type (Ap = aminopyridinate; Ln = lanthanoid metal; X = halide; and n = 1,2,3) is interesting as it provides a good platform for replacing the halide ligands with desired co-ligands. Among rare earth metals, scandium aminopyridinates are rare [14]. Among this class of bulky ligands, (2,6-diisopropylphenyl)-[6-(2,4,6-triisopropylphenyl)-pyridine-2-yl]-amine (Ap\*H) is known to carry the maximum steric bulk with a steric coverage of 3.5 times that of the vastly used pentamethylcyclopentadienyl ligand. We have previously shown that this very bulky aminopyridinato ligand can be used to selectively isolate mono(aminopyridinato) lanthanum species of the [LaAp\*Cl<sub>2</sub>(THF)<sub>3</sub>] type, and we were interested in extending our studies in terms of ionic radii to the smallest scandium metal of the lanthanoid series, and, thus, hereby report our findings [10].



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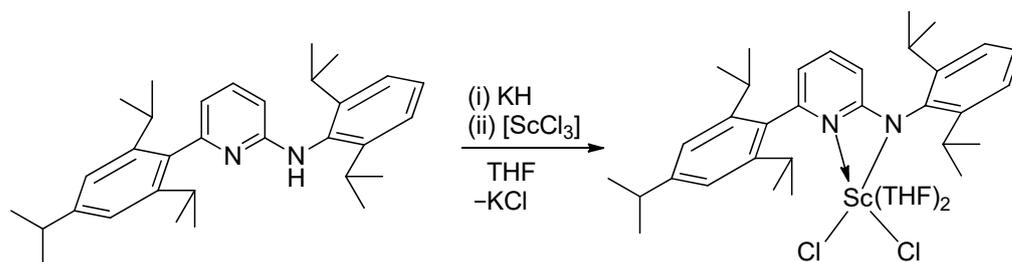
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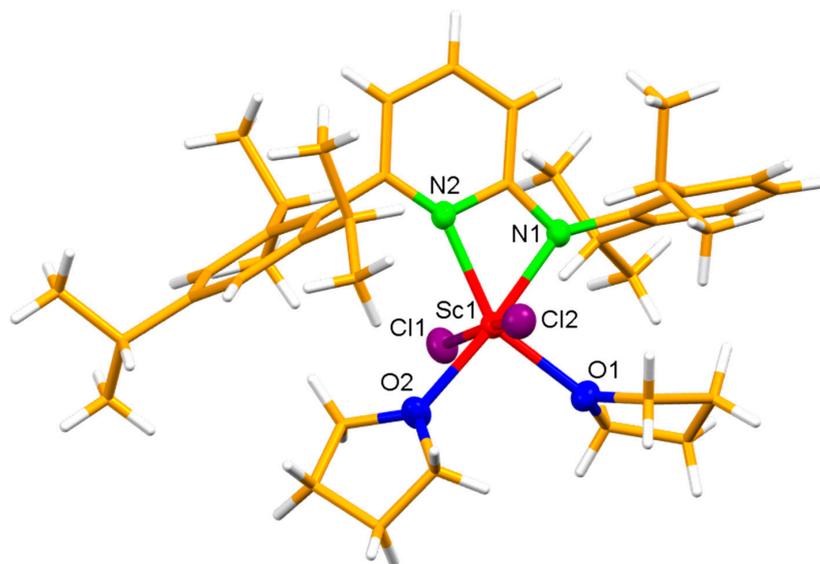
## 2. Results and Discussion

A high yield of the title compound was prepared via a salt elimination reaction. The reaction of  $Ap^*H$  with KH leads to the potassiated aminopyridinate, which can then undergo transmetalation in tetrahydrofuran (Scheme 1) [3]. After workup in hexane, the Sc complex was isolated as a colorless crystalline material with a 70% yield. The formation of the mono(aminopyridinato) complex is quite selective even if excess potassium salt of the ligand reacts with  $[ScCl_3]$ . NMR studies show that two THF molecules are coordinated in contrast to lanthanum, in which three THF molecules were coordinated; -and the corresponding  $\alpha$ - and  $\beta$ - $CH_2$  protons appear at 3.79 and 1.11 ppm, respectively [10]. The  $^1H$  NMR spectrum of the compound exhibits the characteristic splitting pattern of the aminopyridinato ligand, comprising five doublets of the  $CH_3$  protons at 1.13, 1.18, 1.24, 1.44, and 1.58 ppm and two septets for the  $CH(CH_3)_2$  groups at 3.36 and 4.25 ppm in addition to the aromatic signals.



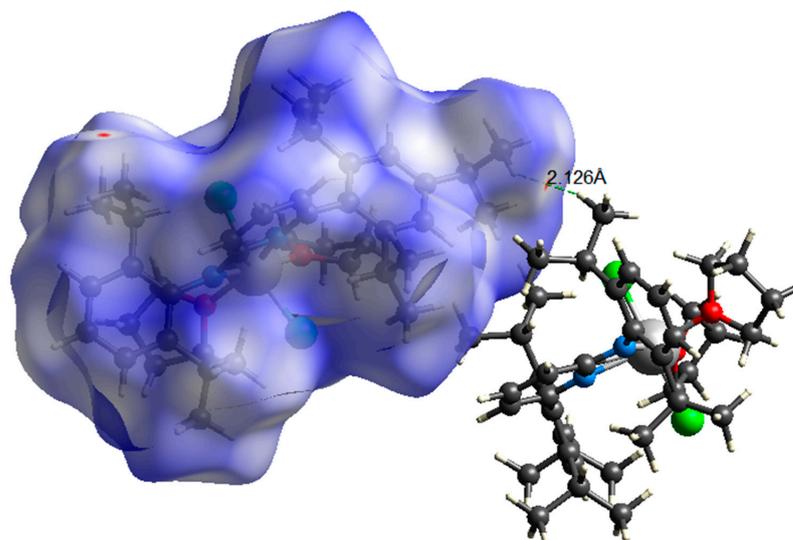
**Scheme 1.** Synthesis of the scandium complex.

The herein-reported Sc complex crystallized in the monoclinic crystal system with the space group  $P2_1/n$ . The solid-state structure shows the monomeric nature of the compound. The coordination around the Sc center is best described as a pseudo-octahedron in which the two chloro ligands occupy the axial positions. The equatorial sites are coordinated by the two oxygen atoms of the THF ligands and the two N-atoms of the aminopyridinato ligand (Figure 1). The distortion is caused by the narrow N–Sc–N angle  $[N1-Sc1-N2\ 61.31(5)^\circ]$ , which leads to either wider  $[O2-Sc1-N2\ 113.20(5)$  and  $N1-Sc1-Cl2\ 95.69(5)^\circ]$  or nearly ideal  $[N1-Sc1-O1\ 89.80(5)^\circ]$  equatorial angles. The herein observed N–Sc–N bite angle is slightly wider than those observed for the isostructural lutetium  $[N-Lu-N\ 58.51(18)^\circ]$  and bis(aminopyridinato) scandium chloride complexes  $[N-Sc-N\ 59.85(19)$  and  $60.57(19)^\circ]$  but identical to that observed for the mono(aminopyridinato) scandium bis(benzyl) complex  $[N-Sc-N\ 61.31(7)^\circ]$  [15–17]. The Cl1–Sc1–Cl2 axial bond angle  $[166.43(2)^\circ]$  is comparable to the lutetium complex  $[Cl1-Lu1-Cl2\ 165.47(7)^\circ]$ . However, a variation is evident for the equatorial bond angles  $[O-Lu-O, N-Lu-O$  and  $O-Lu-N\ 98.95(18), 87.52(17)$  and  $115.03(18)^\circ]$  due to different N–M–N angles. It further leads to wider O–Sc–N *trans*-angles  $[O1-Sc1-N2\ 151.08(5)$  and  $N1-Sc1-O2\ 174.51(5)^\circ]$  than the lutetium complex  $[146.00(16)$  and  $173.53(18)^\circ]$ . The sum of equatorial bond angles is  $360^\circ$ , which indicates that the two oxygen atoms of the THF ligands are nearly coplanar with the pyridine ligand. The two N-atoms show different bond distances to the metal center  $[N1-Sc1\ 2.1491(13)\ \text{\AA}$  and  $N2-Sc1\ 2.2292(13)\ \text{\AA}]$  and, thus, indicate a localization of the anionic function at the amido N-atom. The binding of the aminopyridine to scandium could be best described as a donor functionalized amido metal bond. The  $N_{amido}$ –Sc bond distances of the title compound are comparable, whereas  $N_{pyridine}$ –Sc bond distances are shorter than those reported for the mono-, bis-, and tris(aminopyridinato) scandium complexes [14–16]. These bond lengths are also shorter than those of the isostructural lutetium complex  $[N_{amido}-Lu\ 2.279(5)$  and  $N_{pyridine}-Lu\ 2.3249(5)\ \text{\AA}]$  [17]. The Cl–Sc bond distances  $[2.4216(5)$  and  $2.4295(5)\ \text{\AA}]$  are equivalent but longer than those of bis(aminopyridinato) scandium chloride complexes  $[2.365(2)\ \text{\AA}]$  and shorter than the lutetium complex  $[Cl-Lu\ 2.5212(15)$  and  $2.5312(15)\ \text{\AA}]$  [16,17]. The O–Sc bond distances  $[2.1784(12)$  and  $2.2214(12)\ \text{\AA}]$  show slight variation as previously observed for the mono(aminopyridinato) lutetium dichloride complex  $[2.269(5)$  and  $2.330(4)\ \text{\AA}]$  [17].

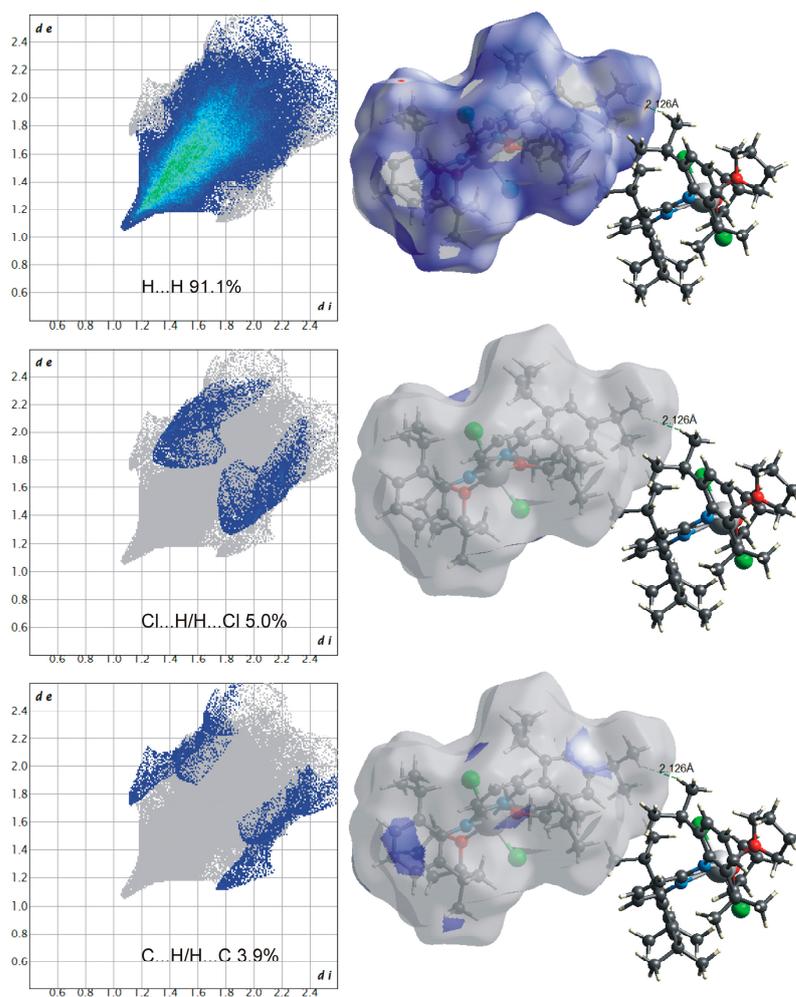


**Figure 1.** Molecular structure of the Sc complex. Ellipsoids are set at 50% probability; selected bond lengths [Å] and angles [°]: N1–Sc1 2.1491(13), N2–Sc1 2.2292(13), O1–Sc1 2.1784(12), O2–Sc1 2.2214(12), Cl1–Sc1 2.4216(5), Cl2–Sc1 2.4295(5); N1–Sc1–O1 89.80(5), N1–Sc1–O2 174.51(5), O1–Sc1–O2 95.69(5), N1–Sc1–N2 61.31(5), O1–Sc1–N2 151.08(5), O2–Sc1–N2 113.20(5), N1–Sc1–Cl1 97.01(4), O1–Sc1–Cl1 93.17(3), O2–Sc1–Cl1 82.81(4), N2–Sc1–Cl1 91.82(4), N1–Sc1–Cl2 95.74(4), O1–Sc1–Cl2 91.49(3), O2–Sc1–Cl2 84.06(4), N2–Sc1–Cl2 90.23(4), and Cl1–Sc1–Cl2 166.43(2).

Hirshfeld surface analyses were used to quantify and visualize any close intermolecular contacts in the complex. For this purpose, the CIF file (supplementary materials) was used as an input file by applying Crystal Explorer 17.50 [18]. In a three-dimensional representation, interactions with normalized contact distance in a crystal structure shorter than the sum of the corresponding van der Waals radii of the atoms have been shown as red spots, and the longer contacts with the positive  $d_{\text{norm}}$  value have been represented as blue (Figure 2) [4]. On the Hirshfeld surfaces, the H···H interactions appeared to be not only the main contributing region (91.1%) but at times seemed to be the strongest and closest interactions [2.126 Å], appearing as dark red spots (Figure 3). The H···C/C···H contacts, due to C—H··· $\pi$  interactions and H···Cl/Cl···H interactions, are the other contributing regions (3.9 and 5.0%, respectively) that could be observed as segregated wing pairs in the fingerprint plots.



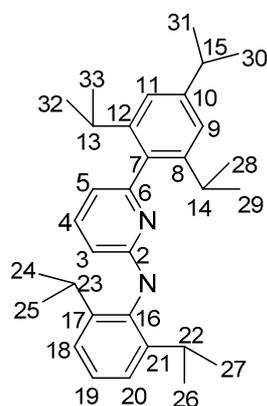
**Figure 2.** View of the three-dimensional Hirshfeld surface of the Sc complex plotted over  $d_{\text{norm}}$  ranging from  $-0.0487$  to  $1.5788$ .



**Figure 3.** Two-dimensional fingerprint plots for all intermolecular contacts in the Sc complex. The percentage of contribution is specified for each contact.

### 3. Experimental

All manipulations were performed with the rigorous exclusion of oxygen and moisture in Schlenk-type glassware on a dual manifold Schlenk line or in an N<sub>2</sub>-filled glove box (mBraun 120-G) with a high-capacity recirculator (<0.1 ppm O<sub>2</sub>). Solvents were dried by distillation from sodium wire/benzophenone. ScCl<sub>3</sub> was purchased from ABCR GmbH. Deuterated solvents were obtained from Cambridge Isotope Laboratories and were degassed, dried, and distilled prior to use. NMR spectrum was recorded on Varian 400 MHz at ambient temperature, and the NMR signals were assigned according to Figure 4. The chemical shifts were reported in ppm relative to the internal TMS. Elemental analyses (CHN) were determined using a Vario EL III instrument. Ap\*H and Ap\*K were synthesized following the literature procedures [3]. An X-ray crystal structure analysis was performed with an STOE-IPDS II equipped with an Oxford Cryostream low-temperature unit. Structure solution and refinement were accomplished using SIR97 [19], SHELXL97 [20], and WinGX [21]. The crystallographic data as collected by single crystal analysis is presented in Table 1. CCDC-2302647 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) accessed on 13 March 2024 or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336-033; e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk).



**Figure 4.** NMR labelling scheme.

**Table 1.** The crystallographic data of the compound.

Empirical Formula	C <sub>40</sub> H <sub>59</sub> Cl <sub>2</sub> N <sub>2</sub> O <sub>2</sub> Sc
Formula weight	715.75
Crystal system	monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>a</i> [Å]	12.4441(8)
<i>b</i> [Å]	22.9975(10)
<i>c</i> [Å]	13.9971(8)
$\alpha$ [deg]	
$\beta$ [deg]	92.297(5)
$\gamma$ [deg]	
<i>V</i> , [Å <sup>3</sup> ]	4002.5(4)
Crystal size, [mm <sup>3</sup> ]	0.3 × 0.3 × 0.2
$\rho_{\text{calcd}}$ , [g cm <sup>-3</sup> ]	1.188
$\mu$ , [mm <sup>-1</sup> ] (Mo K $\alpha$ )	0.351
<i>T</i> , [K]	193(2)
2 $\theta$ range, [deg]	3.40–51.46
No. of reflections (unique)	7530
No. of reflections obs. [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	6557
No. of parameters	424
wR <sup>2</sup> (all data)	0.0966
R-value [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0376

**Synthesis:** Ap\*K (1.49 g, 3 mmol) was added to [ScCl<sub>3</sub>] (0.453 g, 3 mmol) in THF (50 mL) at 0 °C and the reaction solution was stirred for ca. 10 min. The resulting bright yellow solution was then stirred at room temperature for 24 h. THF was evaporated under a vacuum, and the product was dissolved in hexane (30 mL). The solution was filtered, and the filtrate was reduced in a vacuum to ca. one-third, resulting in a colorless product at −25 °C. Yield: 1.5 g (69.8%) C<sub>40</sub>H<sub>59</sub>Cl<sub>2</sub>N<sub>2</sub>O<sub>2</sub>Sc (715.77): Calcd. C 67.12, N 3.91, H 8.31; found C 67.19, N 3.92 H 8.62; <sup>1</sup>H-NMR (250 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): δ = 1.11 (br., 8H, β-CH<sub>2</sub>, THF), 1.13 (d, <sup>3</sup>J(H,H) = 6.8 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.18 (d, <sup>3</sup>J(H,H) = 6.8 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.24 (d, <sup>3</sup>J(H,H) = 6.8 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.44 (d, <sup>3</sup>J(H,H) = 6.8 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.58 (d, <sup>3</sup>J(H,H) = 6.8 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>), 3.36 (sept, <sup>3</sup>J(H,H) = 6.8 Hz, 3H, H-19), 3.79 (br., 8H, α-CH<sub>2</sub>, THF), 4.25 (sept, <sup>3</sup>J(H,H) = 6.8 Hz, 2H, H-13,16), 5.87 (d, <sup>3</sup>J(H,H) = 8.5 Hz, 1H, H-3), 6.12 (d, <sup>3</sup>J(H,H) = 7.1 Hz, 1H, H-5), 6.88 (dd, <sup>3</sup>J(H,H) = 8.5, <sup>3</sup>J(H,H) = 7.1 Hz, 1H, H-4), and 7.18–7.28 (m, 5H, H-9,11,18,19,20) ppm.

#### 4. Conclusions

In conclusion, a rare example of mono(aminopyridinate)scandium chloride has been isolated and completely characterized. NMR studies and X-ray analysis confirm the coordination of two THF molecules. Hirshfeld analyses show that H...H, H...C/C...H and H...Cl/Cl...H are the contributing interactions in the solid-state structure.

**Supplementary Materials:** The <sup>1</sup>H-NMR spectrum, CIF data and molfile of title compound can be downloaded online.

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**Data Availability Statement:** All data generated or analyzed during this study are included in this published article.

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**Conflicts of Interest:** There are no conflicts of interest to declare.

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