

## Synthesis and Electronic Spectra of Fluorinated Aryloxy and Alkoxide $[\text{NiX}_4]^{2-}$ Anions

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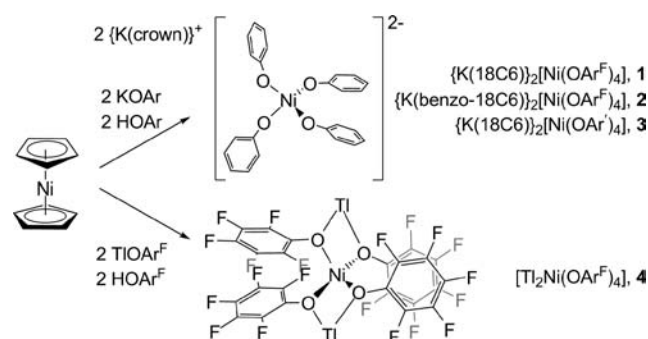
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Five new homoleptic  $[\text{NiX}_4]^{2-}$  compounds have been prepared with the fluorinated ligands  $\text{OC}_6\text{F}_5$  ( $\text{OAr}^{\text{F}}$ ),  $\text{OC}_6\text{H}_3(\text{CF}_3)_2$  ( $\text{OAr}'$ ), and  $\text{OC}_4\text{F}_9$  ( $\text{OR}^{\text{F}}$ ) and characterized with X-ray crystallography, magnetic susceptibility, and elemental analysis. Electronic spectral studies show that these ligands engender a ligand-field environment similar to that of fluoride and thus act electronically like fluoride, but with none of the drawbacks of  $\text{F}^-$  as a transition-metal ligand.

Homoleptic and mononuclear aryloxy complexes of the form  $[\text{M}(\text{OAr})_n]^{m-}$  or analogous alkoxides such as  $[\text{M}(\text{OR})_n]^{m-}$  have proven challenging to synthesize because of the propensity of these ligands to bridge multiple metal centers. Previous work demonstrated that extensive fluorination of aryloxy rings permits the isolation of homoleptic phenolate anions with  $\text{Co}^{\text{II}}$  and  $\text{Cu}^{\text{II}}$ .<sup>1</sup> Under analogous conditions with nonfluorinated phenolate, only low yields of dimeric structures are obtained.<sup>1</sup> Herein we report the extension of this chemistry to  $\text{Ni}^{\text{II}}$  with two fluorinated aryloxides and one fluorinated alkoxide that has resulted in tetrahedral nickel anions surrounded by heavily fluorinated oxygen-donor ligands. UV–vis and near-IR spectroscopic analysis has been carried out to describe these newer ligands in the context of the traditional spectrochemical series.

The homoleptic anions with fluorinated aryloxides of the form  $[\text{Co}(\text{OAr})_4]^{2-}$  and  $[\text{Cu}(\text{OAr})_4]^{2-}$  were readily obtained by metathesis reactions of metal halides  $\text{MX}_2$  with potassium or thallium salts of the appropriate aryloxy anion.<sup>1</sup> Such reactions were unsuccessful in the case of nickel. With  $\text{NiCl}_2$  or  $\text{NiCl}_2(\text{DME})$ , incomplete substitution was observed with either potassium or thallium aryloxy salts, and with  $\text{NiI}_2$ , reduction to  $\text{Ni}^0$  occurred.

**Scheme 1.** Synthesis of Fluorinated Homoleptic Nickel Aryloxy Complexes



An alternative synthesis via the fluorinated phenols  $\text{HOAr}^{\text{F}}$  and  $\text{HOAr}'$  succeeded. Alcoholysis of  $[\text{Cp}_2\text{Ni}]$  with 2 equiv of phenol and 2 equiv of the appropriate aryloxy in tetrahydrofuran at reflux for several days was necessary. As shown in Scheme 1, potassium aryloxides and crown compounds were used to synthesize  $\{\text{K}(18\text{C}6)\}_2[\text{Ni}(\text{OAr}^{\text{F}})_4]$  (**1**),  $\{\text{K}(\text{benzo-18C}6)\}_2[\text{Ni}(\text{OAr}^{\text{F}})_4]$  (**2**),  $\{\text{K}(18\text{C}6)\}_2[\text{Ni}(\text{OAr}')_4]$  (**3**), and thallium aryloxy,  $\text{TIOAr}^{\text{F}}$ , was used for the preparation of  $[\text{Ti}_2\text{Ni}(\text{OAr}^{\text{F}})_4]$  (**4**). The formation of  $\text{Ni}-\text{OAr}$  linkages via alcoholysis is rare but not unprecedented. Previously,  $[\text{Cp}_2\text{Ni}]$  had been reacted with phenols to make phosphine phenolate complexes,<sup>2,3</sup> a bridging phosphide with pendant phenol,<sup>4</sup> and an N-heterocyclic functionalized salen derivative.<sup>5</sup> An earlier report was made of green material isolated from the reaction of  $\text{TIOAr}^{\text{F}}$  and  $\text{NiCl}_2$  in  $\text{CH}_3\text{CN}$  characterized only as having the stoichiometry  $\{\text{Ni}(\text{OAr}^{\text{F}})_2\}$ .<sup>6</sup>

Notably, the metathesis reaction of  $\text{NiI}_2$  and 4 equiv of  $\text{KOR}^{\text{F}}$  works well for the alkoxide case  $\{\text{K}(18\text{C}6)\}_2[\text{Ni}(\text{OR}^{\text{F}})_4]$  (**5**), as depicted in Scheme 2. This result suggests that the sensitivity

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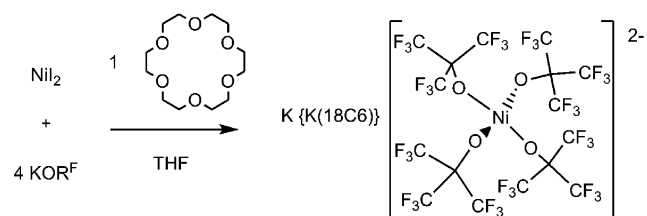
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**Scheme 2.** Synthesis of Homoleptic Nickel Alkoxide Complex **5**

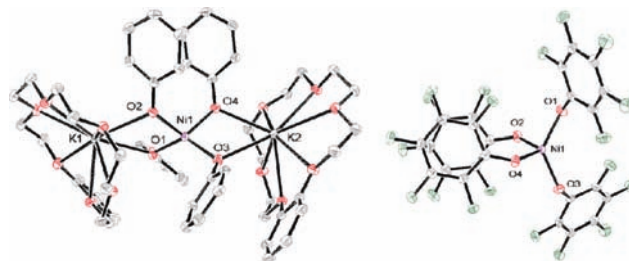
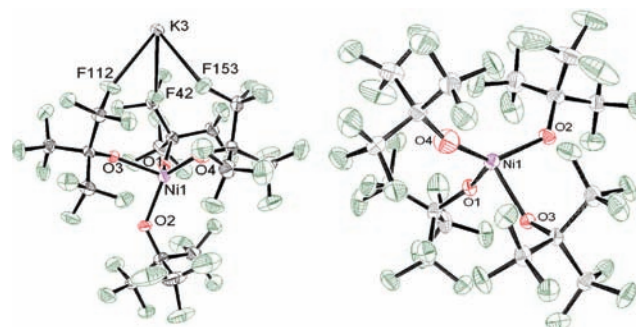
of  $\text{NiI}_2$  to reduction, in the presence of aryloxide but not alkoxide ligands, may be due to the relative ease of oxidation of aryloxide anions versus alkoxide ones.

Repeated attempts to make **5** with 2 equiv of 18C6 were unsuccessful. Purple crystalline material that analyzed as **5** was obtained with some additional colorless material, probably 18C6. We hypothesize that the 3-fold coordination of the uncrowned  $\text{K}^+$  by the three  $\text{CF}_3$  groups, *vide infra*, is more favorable than coordination by the crown ether.

All of the structures of the divalent nickelate complexes **1–5** are approximately tetrahedral at  $\text{Ni}^{\text{II}}$  with  $\{\text{NiO}_4\}$  coordination, except in **4**, where the coordinated Tl atoms create greater distortion. X-ray crystallographic studies were carried out according to the parameters collected in Table S1 of the Supporting Information. Only the connectivity of **1** was obtained from a low-quality data set, but the stoichiometry was confirmed.<sup>7</sup> Within the limits of the data set, the structure of **1** is very similar to that of **2**. The precise interatomic metrical parameters for **2–5** from the diffraction experiments are summarized in Table S2 of the Supporting Information. The X-ray crystal structure of  $\{\text{K}(18\text{C}6)\text{OAr}^{\text{F}}\}$  (**6**) has also been determined for comparison purposes, and an ORTEP is presented in Figure S1 of the Supporting Information.

The structure of compound **2** is tetrahedral at Ni with a dihedral angle between the  $\text{O1–Ni–O2}$  and  $\text{O3–Ni–O4}$  planes of  $85.6^\circ$ . On the left side of Figure 1, the cations and anion are shown, revealing that two O atoms are bridged by an encapsulated  $\{\text{K}(18\text{C}6)\}^+$  cation on each side of the complex. The average  $\text{K–O}_{\text{Ar}}$  distance is  $2.815(13)$  Å, which is longer than the  $\text{K–O}_{\text{Ar}}$  bond distance of  $2.6123(11)$  Å in **6**. The weak interactions between K and the aryloxide O atoms cause the subtended  $\text{O–Ni–O}$  angles to be smaller [average =  $89.0(5)^\circ$ ] than those without bridging K centers [average =  $120(8)^\circ$ ]. The Ni–O distances exhibit a short (average =  $1.934$  Å) and long (average =  $1.948$  Å) distance in each pair bridged by a single K and are slightly longer than other Ni–O bond lengths in  $\{\text{NiO}_4\}$  environments in the CSD,<sup>8</sup> *vide infra*, because of the less basic O atoms. The  $\text{OAr}^{\text{F}}$  ligand has previously been bound as a terminal ligand to Ni in  $[(\text{Ph}_3\text{P})_2\text{Ni}(\text{OAr}^{\text{F}})_2]$  [ $\text{Ni–O} = 1.852(2)$  Å]<sup>9</sup> and as a bridging ligand between two Ni centers in  $[(\text{Ar}^{\text{F}})_2\text{Ni}(\mu_2\text{–OAr}^{\text{F}})_2\text{Ni}(\text{Ar}^{\text{F}})_2]$ ,<sup>10</sup> and  $[\{\text{CpCo}\{\text{P}(=\text{O})(\text{OMe})_2\}_3\}_2\text{Ni}_2(\text{OH}_2)_2(\mu_2\text{–OAr}^{\text{F}})_2]$ .<sup>11</sup>

Compound **3**, depicted in Figure S2 of the Supporting Information, is quite similar structurally to **2** with a slightly smaller dihedral angle of  $82.4^\circ$ . The Ni– $\text{OAr}'$  linkage has

**Figure 1.** ORTEP of **2** (left) with no F atoms and (right) the anion of **2** alone with 50% thermal ellipsoids.**Figure 2.** ORTEP of the anion of **5** (left) with F-chelated  $\text{K}^+$  and (right) alone with 50% thermal ellipsoids.

only been measured previously in  $[(\text{Ph}_3\text{P})_2\text{Ni}(\text{OAr}^{\text{F}})_2]$  [ $\text{Ni–O} = 1.857(2)$  Å].<sup>9</sup>

The unit cell of **4** has two independent  $[\text{Ti}_2\text{Ni}(\text{OAr}^{\text{F}})_4]$  molecules, only one of which is shown in Figure S3 of the Supporting Information, with a  $[\text{Ni}(\text{OAr}^{\text{F}})_4]^{2-}$  core similar to that of **1** and **2**, distorted somewhat by the bridging Tl atoms.

The stoichiometry of **5** includes one  $\{\text{K}(18\text{C}6)\}^+$  cation and one crown-free K per Ni center. The crown-free coordination of  $\text{K}^3$  creates a pseudo-3-fold axis along the  $\text{K}^3 \cdots \text{Ni1}$  vector, as shown in Figure 2. The  $\text{K}^3\text{–Ni1–O4}$  angle is  $165.44(9)^\circ$ , while the other three  $\text{K}^3\text{–Ni1–O}_x$  angles average  $56.5(4)^\circ$ . In the crystal structure, there are three different  $\text{K}^+$  environments, as shown in Figure S4 of the Supporting Information. One  $\{\text{K}(18\text{C}6)\}^+$  unit, containing  $\text{K}^2$ , bridges two  $[\text{Ni}(\text{OR}^{\text{F}})_4]^{2-}$  anions via two bridging fluoride atoms F31. Another  $\{\text{K}(18\text{C}6)\}^+$  unit containing  $\text{K}^1$  is not closely bound to any other moiety in the crystal lattice. The two remaining  $\text{K}^+$  ions,  $\text{K}^3$ , are coordinated by three O atoms,  $\text{O1–O3}$ , from the alkoxide ligands and six F atoms from adjacent perfluoro-*tert*-butyl groups, shown on the right side of Figure S4 of the Supporting Information. There are no previous reports of compounds containing the  $\text{NiOR}^{\text{F}}$  unit.

There are only a few other examples of structurally characterized  $\{\text{NiO}_4\}$  coordination in the literature, and all contain  $\text{Ni}^{\text{II}}$  that is part of one or more chelate rings, with an average Ni–O bond distance in the CSD of  $1.87(7)$  Å. The majority of the examples are derivatives of nickel

(7)  $P\bar{1}$ ,  $a = 13.383(6)$  Å,  $b = 13.508(6)$  Å,  $c = 18.540(8)$  Å,  $\alpha = 82.676(6)^\circ$ ,  $\beta = 81.787(6)^\circ$ ,  $\gamma = 73.522(6)^\circ$ .

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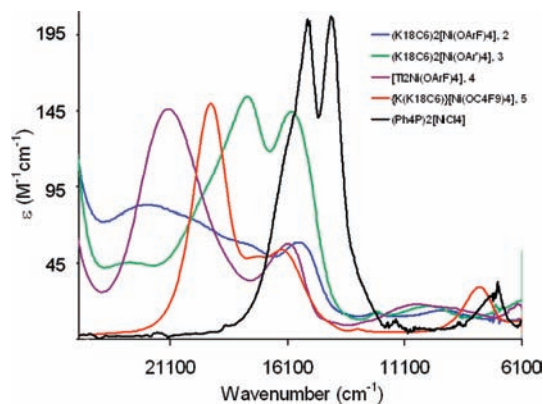
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## COMMUNICATION

bis(acetylacetonate),<sup>12–19</sup> some bis(*o*-catecholate) compounds,<sup>20,21</sup> a few bimetallic species with bridging alkoxides,<sup>22–25</sup> two salicylaldehyde complexes,<sup>26,27</sup> two bridging aryloxides,<sup>28,29</sup> and one polyoxometallate<sup>30</sup> complex.

Previously studied (pseudo)halogen  $[\text{NiX}_4]^{2-}$  complexes with  $D_{2d}$  symmetry have magnetic moments in the range 3.5–4.0  $\mu_B$ . The compounds **1–5** are paramagnetic, with an average  $\mu_{\text{eff}}$  of 3.51  $\mu_B$  for the  $\text{K}_2\text{NiX}_4$  species, as determined by Evans' method at room temperature.<sup>31,32</sup> These values are closest to that for  $[\text{NiCl}_4]^{2-}$ , 3.49  $\mu_B$ , and, in combination with UV–vis data, suggest that the fluorinated aryloxide and alkoxide ligands are among the stronger ligands in the “weak-field” manifold. Figgis has termed these ligands “medium field”<sup>33</sup> in which there is more spin–orbit coupling, and more free-ion-like behavior, consistent with the Racah parameters obtained experimentally, *vide infra*.

The UV–vis–near-IR spectra of compounds **2–5** as well as that of  $[\text{NiCl}_4]^{2-}$  are shown in Figure 3, and their absorption energies are compared with previously published data according to the method of Lever<sup>34,35</sup> to obtain values for the Racah parameter  $B$  and the ligand-field parameter  $D_q$ . All four spectra of the nickel complexes with fluorinated ligands show significantly blue-shifted spectra, compared to  $[\text{NiCl}_4]^{2-}$ , indicating a stronger ligand field. The strongly electron-withdrawing and reduced  $\pi$ -basic character of the ligands results in a large ligand-field splitting, as described by  $D_q$ . The large Racah parameter  $B$  for **5** indicates strong interelectronic repulsion and primarily  $\sigma$ -donor character



**Figure 3.** UV–vis–near-IR spectra of  $[\text{NiX}_4]^{2-}$  species.

**Table 1.** Electronic Spectral Data and Ligand-Field Parameters

$[\text{NiX}_4]^{2-}$	$E(\nu_3)$ ( $\text{cm}^{-1}$ )	$E(\nu_2)$ ( $\text{cm}^{-1}$ )	$B$ ( $\text{cm}^{-1}$ )	$D_q$ ( $\text{cm}^{-1}$ )	ref
$[\text{Ni}(\text{NCO})_4]^{2-}$	16 200	9460	511	311	34, 36
$[\text{NiCl}_4]^{2-}$	14 760	7470	405	206	34, 37
$[\text{NiBr}_4]^{2-}$	13 320	6995	379	201	34, 37
$[\text{Ni}(\text{OAr}^F)_4]^{2-}$ , <b>2</b>	16 660	9290	877	502	this work
$[\text{Ni}(\text{OAr}')_4]^{2-}$ , <b>3</b>	16 820	10,000	867	540	this work
$[\text{Ni}(\text{OAr}^F)_4]^{2-}$ , <b>4</b>	16 000	10400	800	560	this work
$[\text{Ni}(\text{OR}^F)_4]^{2-}$ , <b>5</b>	19 300	7840	1096	427	this work

from the ligand. On the basis of these data, we write the following abbreviated spectrochemical series:



These data demonstrate that the fluorinated aryloxide and alkoxide ligands are as strong in ligand-field terms as fluoride. Unlike fluoride, however, these ligands are much less prone to bridging, as complexes **1–3** and **5** attest. Thus, these ligands serve as an electronic equivalent of fluoride and are therefore expected to stabilize oxidation states for Ni higher than  $\text{Ni}^{2+}$ . A cyclic voltammogram (CV) of **5** with  $E_{\text{pa}}$  of  $-0.2$  V vs  $\text{Ag}/\text{Ag}^+$  is shown in Figure S5 of the Supporting Information.

In summary, several new homoleptic tetrahedral nickelate complexes  $[\text{Ni}(\text{OAr})_4]^{2-}$  and  $[\text{Ni}(\text{OR})_4]^{2-}$  with extensively fluorinated aryloxide and alkoxide ligands have been prepared. Ligand-field studies show that these ligands are best described as “medium-field” and therefore are well positioned to stabilize high-oxidation-state molecules for potential use in C–H activation chemistry because of the ligand field generated and the highly oxidation-resistant ligands themselves.

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**Supporting Information Available:** Full experimental details, tabulated X-ray crystallographic information (Tables S1 and S2) for compounds **2–6**, ORTEPs for compounds **3–6** (Figures S1–S4), a CV of **5** (Figure S5), and time-of-flight electrospray ionization mass spectrometry analysis of **4** (Figure S6). This material is available free of charge via the Internet at <http://pubs.acs.org>. IC9003593

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