

Unravelling the Role of the Pentafluoroorthotellurate Group as a Ligand in Nickel Chemistry

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Abstract: The pentafluoroorthotellurate group (teflate, OTeF_5) is able to form species, for which only the fluoride analogues are known. Despite nickel fluorides being widely investigated, nickel teflates have remained elusive for decades. By reaction of $[\text{NiCl}_4]^{2-}$ and neat ClOTeF_5 , we have synthesized the homoleptic $[\text{Ni}(\text{OTeF}_5)_4]^{2-}$ anion, which presents a distorted tetrahedral structure, unlike the polymeric $[\text{NiF}_4]^{2-}$. This high-spin complex has allowed the study of the electronic properties of the teflate group, which can be classified as a weak/

medium-field ligand, and therefore behaves as the fluoride analogue also in ligand-field terms. The teflate ligands in $[\text{NEt}_4]_2[\text{Ni}(\text{OTeF}_5)_4]$ are easily substituted, as shown by the formation of $[\text{Ni}(\text{NCMe})_6][\text{OTeF}_5]_2$ by dissolving it in acetonitrile. Nevertheless, careful reactions with other conventional ligands have enabled the crystallization of nickel teflate complexes with different coordination geometries, i.e. $[\text{NEt}_4]_2[\text{trans-Ni}(\text{OEt})_2(\text{OTeF}_5)_4]$ or $[\text{NEt}_4][\text{Ni}(\text{bpyMe}_2)(\text{OTeF}_5)_3]$.

Introduction

Nickel fluorides and the related fluoronickelates have been known for decades and their chemistry has been thoroughly studied.^[1] These species form a very special class of compounds, which significantly differ from the heavier nickel halides in mainly two aspects: firstly, the oxidation state +IV is only accessible with fluorides in the well-known $[\text{NiF}_6]^{2-}$, as well as in the unstable and strong oxidizer NiF_4 formed therefrom; secondly, the structures of the different halonickelates in the most common oxidation state +II are different. Whereas the $[\text{NiX}_4]^{2-}$ anions (X = Cl, Br, I) are commonly tetrahedral molecules, $[\text{NiF}_4]^{2-}$ forms layers containing $\{\text{NiF}_6\}$ octahedra connected by shared corners (i.e. bridging fluorides), therefore adopting a structure comparable to that of SnF_4 .^[2] Although more unusual, nickelates containing heavier halides and Ni centers with octahedral coordination are also known, such as $[\text{Ni}_3\text{Cl}_{12}]^{2-}$.^[3]

Within this context, one very interesting analogue of the fluoride is the pentafluoroorthotellurate group (teflate, OTeF_5),

since it is also highly electronegative, yet shows a high steric demand.^[4] These properties, together with its high charge delocalization and robustness against electrophiles and oxidizers make it a unique ligand, able to stabilize species that are usually the only known analogues of the corresponding fluorides. However, in contrast to the fluoride, it is much less prone to acting as a bridging ligand.^[4,5] The teflate group has allowed the isolation of a wide range of weakly coordinating anions,^[6] for example $[\text{Al}(\text{OTeF}_5)_4]^-$,^[7] as well as transition-metal complexes in high oxidation states, as in $\text{Mo}(\text{OTeF}_5)_6$ ^[8] and highly reactive species, such as $[\text{XeOTeF}_5][\text{Sb}(\text{OTeF}_5)_6]$.^[9] Interestingly, in comparison to the high number of main-group teflate species, transition-metal teflate complexes are less abundant, and are mainly known with early transition metals.^[4,5]

In the particular case of nickel, the coordination of the teflate ligand has remained elusive for decades. The reaction of $[\text{NiCl}_2(\text{dppe})]$ (dppe = 1,2-bis(diphenylphosphino)ethane) and $[\text{Ag}(\text{OTeF}_5)(\text{toluene})_2]$ only led to metallic deposits, similarly to other phosphine complexes of group 10 metals.^[10] This behavior was attributed to the redox incompatibility between the teflate and the phosphine ligands, which was disproved by the synthesis of $[\text{Pt}(\text{OTeF}_5)_2(\text{PEt}_3)_2]$.^[11] The homoleptic anion $[\text{Ni}(\text{OTeF}_5)_4]^{2-}$ was mentioned in a review in 1993 as a potential weakly coordinating anion, yet no experimental details were provided, not even years later.^[12] In fact, it was not until 2018 that the first and only nickel teflate complexes were reported by our group, i.e. $[\text{Ni}(\text{OTeF}_5)_2(\text{Hacac})_2]$ and *cis*- $[\text{Ni}(\text{IPrIm})_2(\text{OTeF}_5)_2]$ (acac = acetylacetonate, ^{IPrIm} = 1,3-bis(isopropyl)imidazolin-2-ylidene).^[13]

Since the Pd(II) analogue $[\text{Pd}(\text{OTeF}_5)_4]^{2-}$ is known,^[14,15] and other homoleptic $\{\text{NiO}_4\}$ anions have been also prepared,^[16–18] we envisioned that salts of the $[\text{Ni}(\text{OTeF}_5)_4]^{2-}$ anion should be also stable. Herein we present the synthesis, characterization and study of the hitherto unknown $[\text{Ni}(\text{OTeF}_5)_4]^{2-}$ anion, which has been prepared by using neat ClOTeF_5 as a teflate-transfer

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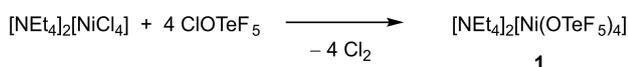
reagent. The extensive use of Ni(II) species to study fundamental properties in coordination chemistry made this compound especially suited to undertake an unprecedented study of the ligand-field properties of the teflate group. The OTeF_5 ligands in this complex can be easily substituted, but a careful choice of ligands and reaction conditions leads to nickel teflate complexes with different coordination geometries.

Results and Discussion

Synthesis and characterization of $[\text{NETe}_4]_2[\text{Ni}(\text{OTeF}_5)_4]$

Various attempts to prepare salts of the $[\text{Ni}(\text{OTeF}_5)_4]^{2-}$ anion by modifying previous synthetic procedures of related species were unsuccessful. Contrary to the usefulness of PdCl_2 as a starting material for the synthesis of the analogous $[\text{Pd}(\text{OTeF}_5)_4]^{2-}$ anion,^[14,15] NiCl_2 proved to be unreactive. Considering the low solubility of this compound, we tried the reaction of different $[\text{NiX}_4]^{2-}$ salts ($\text{X}=\text{Cl}, \text{Br}, \text{I}$) with AgOTeF_5 , but only incomplete substitutions and mixtures of species were obtained. Similar results were found when using $[\text{NiBr}_2(\text{dme})]$ ($\text{dme}=1,2\text{-dimethoxyethane}$) and $[\text{NMe}_4][\text{OTeF}_5]$ or AgOTeF_5 as starting materials, unlike in case of the recently reported synthesis of $[\text{Ni}(\text{OC}_4\text{F}_9)_4]^{2-}$ using $\text{Na}[\text{OC}_4\text{F}_9]$.^[16] Although the use of nickelocene proved to be useful for the synthesis of $[\text{Ni}(\text{OR})_4]^{2-}$ anions ($\text{R}=\text{C}_6\text{F}_5, \text{C}_6\text{H}_3(\text{CF}_3)_2, \text{C}_4\text{F}_9$),^[18] in our case the reaction of nickelocene, HOTeF_5 and $[\text{NMe}_4][\text{OTeF}_5]$ only led to mixtures of unidentified products which could not be separated.

Given the low solubility of Ni halides and the low coordinating ability of the teflate ligand, we envisioned a solvent-free synthesis of the $[\text{Ni}(\text{OTeF}_5)_4]^{2-}$ anion by using neat ClOTeF_5 as the teflate-transfer reagent.^[19] The reaction of $[\text{NETe}_4]_2[\text{NiCl}_4]$ with an excess of ClOTeF_5 leads to the release of Cl_2 and concomitant formation of a dark brown slurry, which upon removal of all volatiles under dynamic vacuum resulted in a dark blue powder (Scheme 1). The transformation takes place quantitatively to yield $[\text{NETe}_4]_2[\text{Ni}(\text{OTeF}_5)_4]$ (1) as a pure substance, as demonstrated by mass balance and elemental analysis. On the other hand, the formation of chlorine was proved by gas-phase UV-Vis spectroscopy (see Figure S1). The isolated compound is extremely moisture-sensitive, but under strict inert conditions, it is thermally stable and decomposes only above 220°C , as determined by thermogravimetric analysis (see Figure S10). Interestingly, the analogous reaction between neat ClOTeF_5 and NiCl_2 does not take place, probably due to the high stability of the highly ionic nickel species. This behavior is in contrast with that of FeCl_3 , which is known to react with ClOTeF_5 in SO_2ClF or $\text{C}_4\text{F}_9\text{SO}_2\text{F}$ to yield $\text{Fe}(\text{OTeF}_5)_3$.^[20]



Scheme 1. Synthesis of $[\text{NETe}_4]_2[\text{Ni}(\text{OTeF}_5)_4]$ (1).

Contrary to HOTeF_5 , AgOTeF_5 or $\text{B}(\text{OTeF}_5)_3$, which have been extensively used in the synthesis of teflate derivatives,^[4,5] the hypochlorite ClOTeF_5 has resulted to be of limited use and only a few derivatives have been prepared therefrom.^[8,20,21] In our case, the use of the neat substance and the need of no solvent is the key factor leading to a successful reaction for two reasons. Firstly, it allows to circumvent the need of easily accessible and soluble nickel precursors, the latter being an important drawback for nickel halides. Secondly, the resulting compound is unstable in donor solvents such as MeCN (see below).

Crystals of $[\text{NETe}_4]_2[\text{Ni}(\text{OTeF}_5)_4]$ (1) suitable for X-ray diffraction were grown by slow evaporation of a saturated solution of the compound in *ortho*-difluorobenzene (*o*DFB) at room temperature. Compound 1 crystallizes in the monoclinic space group $P2_1/c$ (Figure 1). The coordination geometry of the $[\text{Ni}(\text{OTeF}_5)_4]^{2-}$ anion can be described as a distorted tetrahedron, as becomes clear from the O–Ni–O angles, which range between $90.9(3)$ and $138.4(3)^\circ$. The deviation from the 109.5° in a regular tetrahedron becomes much more prominent than in the related salt $[\text{NETe}_4]_2[\text{NiCl}_4]$, where angles are in the narrow range $106.83(14)\text{--}110.81(7)^\circ$.^[22] To describe the distortions found in four-coordinate complexes in a more objective way, the geometry parameter τ_4 was developed by Houser et al.^[23] A perfect tetrahedral geometry would present a value of $\tau_4=1$, which is almost the case for the $[\text{NiCl}_4]^{2-}$ anion (0.98). In our case, the τ_4 parameter for the $[\text{Ni}(\text{OTeF}_5)_4]^{2-}$ anion has a value of 0.75, which shows clearly the distortion. The distortion of compound 1 is most probably due to electronic rather than to steric reasons, as the related $[\text{NETe}_4][\text{Al}(\text{OTeF}_5)_4]$ salt, which shows much shorter Al–O bond lengths ($175.0(14)\text{--}178.8(13)$ pm), is

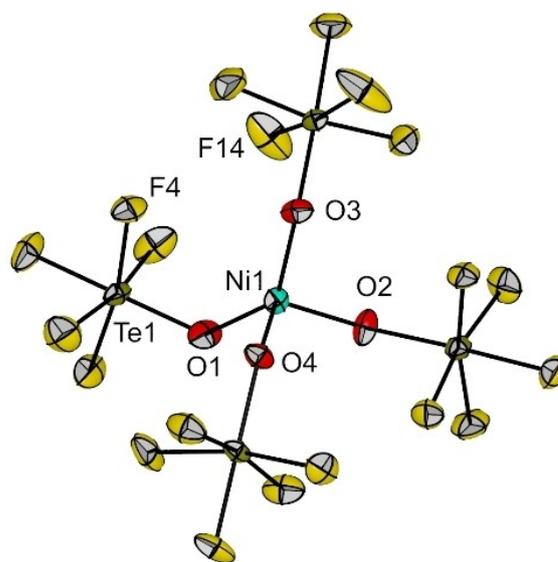


Figure 1. Molecular structure of the $[\text{Ni}(\text{OTeF}_5)_4]^{2-}$ anion in the solid state as found in crystals of 1. The $[\text{NETe}_4]^+$ cations have been omitted for clarity. Displacement ellipsoids set at 50% probability. Selected bond lengths [pm] and angles [$^\circ$]: Ni1–O1 195.2(7), Ni1–O2 194.2(7), Ni1–O3 195.5(7), Ni1–O4 193.2(6), O1–Ni1–O2 96.6(3), O1–Ni1–O3 138.4(3), O1–Ni1–O4 107.8(3), O2–Ni1–O3 108.7(3), O2–Ni1–O4 115.3(3), O3–Ni1–O4 90.9(3). For crystallographic details see Supporting Information.

less distorted.^[24] In fact, a careful analysis of the Ni...F intramolecular interactions in the solid state shows that the distances Ni1–F4 (321.6(7) pm) and Ni–F14 (321.3(7) pm) are much shorter than the average Ni...F contacts. These interactions might have a key role in the distortion of the ideal tetrahedral geometry found in the $[\text{Ni}(\text{OTeF}_5)_4]^{2-}$ anion, as the largest O1–Ni1–O3 angle (138.4(3)°) is the one that involves the teflate ligands to which F4 and F14 belong (see Figure 1). Interestingly, only one additional tetrahedrally coordinated teflate dianion complex has been characterized by single-crystal X-ray diffraction, i.e. $[\text{Hg}(\text{OTeF}_5)_4]^{2-}$, which also shows a significant distortion (bond angles ranging from 86.3(2) to 125.9(3)°).^[25]

Interestingly, this is one of the few reported crystal structures of a Ni(II) compound with a $\{\text{NiO}_4\}$ coordination, which contains only monodentate ligands.^[17,18] Additionally, it is the only one in which the oxygen atoms do not establish strong interactions with a metal cation, as observed, for instance, in $\{\text{K}(\text{18C6})\}_2[\text{Ni}(\text{OC}_6\text{F}_5)_4]^{18}$ or in $[\text{Na}(\text{dme})_2][\text{Ni}(\text{OC}(\text{CF}_3)_3)_4]^{16}$. It is also interesting to note, that in the structure of the palladium analogue, which shows a planar $\{\text{PdO}_4\}$ coordination, the O atoms of the teflate ligands are bonded to Ag(I) ions.^[14,15] The Ni–O bond lengths, however, are in the range of other tetrahedral Ni(II) complexes with a $\{\text{NiO}_4\}$ environment.^[18] Interestingly, all halide complexes $[\text{NiX}_4]^{2-}$ (X = Cl, Br, I) show a tetrahedral geometry except $[\text{NiF}_4]^{2-}$, which shows an extended structure consisting of layers of corner-sharing $\{\text{NiF}_6\}$ octahedral units in $\text{K}_2[\text{NiF}_4]$.^[26] Therefore, $[\text{NEt}_4]_2[\text{Ni}(\text{OTeF}_5)_4]$ (1) arises as an analogue of $[\text{NiF}_4]^{2-}$ with a discrete structure instead of a polymeric one.

The IR spectrum of $[\text{NEt}_4]_2[\text{Ni}(\text{OTeF}_5)_4]$ shows the two most characteristic stretching vibrations of the teflate ligand (see Figure S3): the Te–F vibration appears at 662 cm^{-1} , whereas the Te–O one at 834 cm^{-1} . As the latter appears above 820 cm^{-1} , the Ni–O bonds can be considered to have an ionic character,^[27] although it is far away from the highest reported Te–O vibration, i.e. 873 cm^{-1} in $\text{Cs}[\text{OTeF}_5]$,^[28] or 867 cm^{-1} in $[\text{N}^t\text{Bu}_4][\text{OTeF}_5]$, where the teflate group seems not to be so affected by the positive charge.^[29]

For tetrahedral complexes such as 1, typically high-spin configurations are observed.^[30] In the case of a d^8 system as it is the case in $[\text{Ni}(\text{OTeF}_5)_4]^{2-}$, this leads to a $S=1$ state, which implies the existence of two unpaired electrons. Accordingly, only two broad signals of very poor quality due a bad signal-to-noise ratio appear in the ^{19}F NMR in CD_2Cl_2 , which is in line with the coordination of the teflate ligands to a paramagnetic Ni(II) center. Therefore, we decided to investigate the magnetism of $[\text{NEt}_4]_2[\text{Ni}(\text{OTeF}_5)_4]$ (1). We used two different techniques to determine the effective magnetic moment of 1 at room temperature (see Supporting Information for details). By using the magnetic susceptibility balance, the effective magnetic moment was determined to be $\mu_{\text{eff}}=3.62\ \mu_{\text{B}}$, whereas with a SQUID magnetometer a value of $\mu_{\text{eff}}=3.92\ \mu_{\text{B}}$ was obtained. The latter was found, as expected, to be independent of the temperature (Figure 2). These values are somewhat higher than the spin-only value of $\mu_{\text{eff}}=2.83\ \mu_{\text{B}}$, calculated for two unpaired electrons. This deviation can be rationalized by orbital contribu-

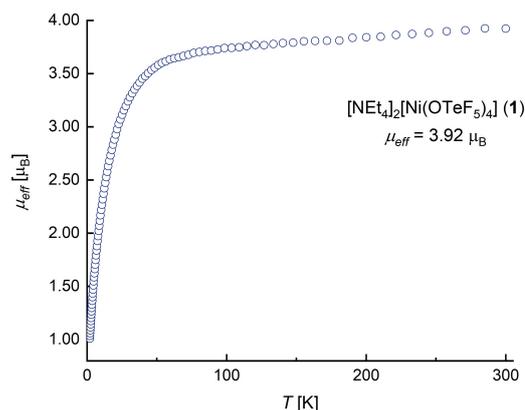


Figure 2. μ_{eff} versus T plot for compound $[\text{NEt}_4]_2[\text{Ni}(\text{OTeF}_5)_4]$ (1), obtained with a SQUID magnetometer.

tions due to the tetrahedral structure and low ligand field strength. The observed value of the effective magnetic moment, according to the approximations provided by Figgis,^[31] lies in the range of values expected for tetrahedral nickel(II) complexes with weak-field and medium-field ligands and hence it classifies the pentafluoroorthotellurate as belonging to this ligand class. In fact, the $[\text{NiX}_4]^{2-}$ anions (X = Cl, Br, I) also show effective magnetic moments in the range of $3.5\text{--}3.9\ \mu_{\text{B}}$.^[32] Additionally, other fluorinated alkoxide and aryloxy ligands provide values in the lower part of the range, and were therefore classified also as medium-field ligands.^[18]

Ligand-field properties of the OTeF_5 group

Electronic spectroscopy of d metal complexes is useful for the study of structural and bonding properties of coordination compounds.^[33] Nickel(II) complexes have been widely used to study the electronic properties of d^8 ions, which can exist in different coordination geometries.^[34] Nevertheless, in the case of tetrahedral complexes, the combination of Ni^{II} with fluoride ligands could not be studied, as the homoleptic tetrafluoronickelate(II) aggregates to yield higher coordination numbers (see above). The teflate group is known to have comparable electron-withdrawing properties to the fluoride, as stated in the introduction, and surprisingly, its electronic properties in coordination chemistry have not been reported thus far. The $[\text{Ni}(\text{OTeF}_5)_4]^{2-}$ anion arises then as a suitable option to undertake such study due to its discrete structure.

The UV-Vis-near-IR spectrum of $[\text{NEt}_4]_2[\text{Ni}(\text{OTeF}_5)_4]$ ($\sim 0.01\text{ M}$ in CH_2Cl_2) is shown in Figure 3. The two important main bands ν_2 and ν_3 are observed. The former appears at 8511 cm^{-1} , whereas the latter consists of two components at 17452 cm^{-1} and 15873 cm^{-1} . From them, the values of the ligand-field parameter Dq and the Racah parameter B can be calculated according to the equations published by Dou (see Supporting Information for details).^[35] In our tetrahedral d^8 species, which has a T_1 ground state, these parameters are calculated to be $Dq=461\text{ cm}^{-1}$ and $B=896\text{ cm}^{-1}$, respectively.

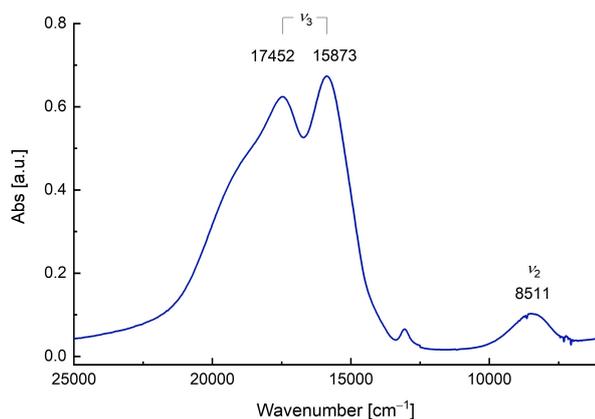
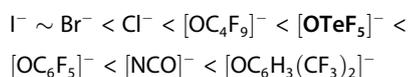


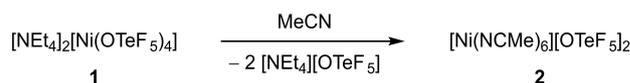
Figure 3. UV-Vis-near-IR spectrum of $[\text{NEt}_4]_2[\text{Ni}(\text{OTeF}_5)_4]$ (1) in CH_2Cl_2 (~ 0.01 M).

The spectrochemical series empirically ranks the ligands according to the intensity of the crystal field they create. In terms of the ligand-field theory, the teflate ligand also behaves similarly to fluoride, as it leads to a greater ligand-field splitting Dq than the chloride in the analogous $[\text{NiCl}_4]^{2-}$. Additionally, with its strong electron-withdrawing character, it produces a similar energy difference between the d orbitals, which is comparable to other fluorinated ligands, such as $[\text{OC}_4\text{F}_9]^-$ or $[\text{OC}_6\text{F}_5]^-$ (Table 1).^[18] The teflate can be included in the spectrochemical series in a similar position as the fluoride, therefore both being comparably strong ligands in ligand-field terms:



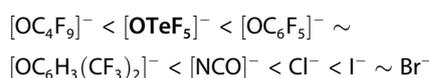
According to its location in the spectrochemical series, it can be classified as a weak/medium-field ligand, as was also concluded from the determined effective magnetic moment of the $[\text{Ni}(\text{OTeF}_5)_4]^{2-}$ anion (see above).

Furthermore, the Racah parameter B indicates the repulsion of d electrons in a metal.^[33] In comparison to the gaseous free ion, this parameter decreases upon coordination of ligands, indicating a decrease in the interelectronic repulsion in complexes. This reduction of the B parameter is the so-called



Scheme 2. Dissociation of the $[\text{OTeF}_5]^-$ in complex 1 upon dissolving in acetonitrile to yield $[\text{Ni}(\text{NCMe})_6][\text{OTeF}_5]_2$ (2).

nephelauxetic effect, which depends both on the metal and the ligands.^[38] For a given metal, within the series of halides, the fluoride ligand usually leads to the least repulsion between d electrons, which implies that the B parameter associated with it is the largest of all of them. Also the teflate ligand shows a B parameter, which is larger than the parameters of the heavier halides (Table 1). However, it is actually similar to those of related O-donor ligands, which is in agreement with the higher electronegativity of oxygen (in comparison with chloride and the heavier halides), therefore reducing further the interelectronic repulsion of the d electrons.^[33] This allows to include the teflate group in the nephelauxetic series of ligands, in order of decreasing B parameter (and increasing nephelauxetic effect), as follows:



Chemical behavior of $[\text{NEt}_4]_2[\text{Ni}(\text{OTeF}_5)_4]$

As commented previously, compound $[\text{NEt}_4]_2[\text{Ni}(\text{OTeF}_5)_4]$ (1) is very sensitive to humidity, which gives clear evidence of the high lability of the Ni–OTeF₅ bonds. In fact, when the compound is dissolved in a coordinating solvent, the teflate ligands are rapidly and completely dissociated, whereas the Ni(II) center becomes solvated. This shows that the $[\text{OTeF}_5]^-$ group behaves as a weakly coordinating ligand. For instance, upon addition of acetonitrile, the characteristic deep blue color of $[\text{NEt}_4]_2[\text{Ni}(\text{OTeF}_5)_4]$ (1) disappears, giving rise to the typical pale blue color of the octahedrally-coordinated $[\text{Ni}(\text{NCMe})_6]^{2+}$ (Scheme 2). In fact, the solution of compound 1 in CD_3CN allows to observe the signals corresponding to the free $[\text{OTeF}_5]^-$ anion in the ¹⁹F NMR spectrum,^[29] showing the AB₄ pattern typical for

Table 1. Electronic spectral data and ligand-field parameters of the $[\text{Ni}(\text{OTeF}_5)_4]^{2-}$ anion and related species.^[a]

| Compound | ν_2 [cm^{-1}] | ν_3 [cm^{-1}] ^[b] | Dq [cm^{-1}] | B [cm^{-1}] | Conditions |
|--|------------------------------|---|---------------------------|--------------------------|--|
| $[\text{Ni}(\text{OTeF}_5)_4]^{2-}$ | 8511 | 15873, 17452 | 461 | 896 | CH_2Cl_2 (~ 0.01 M) |
| $[\text{NiCl}_4]^{2-}$ | 7549 | 14250, 15240 | 409 | 795 | MeCN (0.01 M) ^[34,36] |
| $[\text{NiBr}_4]^{2-}$ | 6995 | 13230, 14140 | 379 | 738 | MeCN (0.01 M) ^[34,36] |
| $[\text{NiI}_4]^{2-}$ | 7042 | 14030 | 382 | 760 | MeNO_2 (0.01 M) ^[34,36] |
| $[\text{Ni}(\text{NCO})_4]^{2-}$ | 9460 | 15600, 16800 | 511 | 841 | MeNO_2 (0.036 M) ^[34,37] |
| $[\text{Ni}(\text{OC}_4\text{F}_9)_4]^{2-}$ | 7840 | 19300 | 427 | 1096 | CH_2Cl_2 ^[18] |
| $[\text{Ni}(\text{OC}_6\text{F}_5)_4]^{2-}$ | 9290 | 16660 | 502 | 877 | CH_2Cl_2 ^[18] |
| $[\text{Ni}(\text{OC}_6\text{H}_3(\text{CF}_3)_2)_4]^{2-}$ | 10000 | 16820 | 540 | 868 | CH_2Cl_2 ^[18] |

[a] All values of Dq and B have been calculated for this work according to the equations published by Dou,^[35] by using the values of ν_2 and ν_3 which are provided in the corresponding entry (see Supporting Information for details). [b] ν_3 was estimated to be the average of the two components observed for such absorption, when this was the case.

OTeF₅ groups, but with a rather poor quality due to the paramagnetism of the cation (see Figure S2). A similar behavior was reported for the complex [Ni(OTeF₅)₂(Hacac)₂] in acetonitrile,^[13] as well as for the neutral Ni[EF₆]₂ species (E = Bi, Sb),^[39] which form the corresponding [Ni(NCMe)₆][EF₆]₂ salts upon dissolving in acetonitrile. In related nickel pentafluoroosulfate compounds, the OSF₅ ligand was also suggested to undergo dissociation upon dissolving in acetonitrile.^[40]

Slow gas diffusion of Et₂O into an acetonitrile solution of compound **1** at low temperature allowed to obtain purple single crystals of [Ni(NCMe)₆][OTeF₅]₂ (**2**), which proves the described behavior (see Figure 4). The IR spectrum of **2** (see Figure S4) clearly shows the bands corresponding to the [Ni(NCMe)₆]²⁺ cation^[39] and to the [OTeF₅]⁻ anion.^[29]

This salt crystallizes in the trigonal space group *R*-3. Both the cation and the anions have octahedral geometry. When focusing on the [Ni(NCMe)₆]²⁺ cation, it can be noticed that it is a distorted octahedron, with similar structural parameters as those found in the related [Ni(NCMe)₆][SbF₆]₂.^[41] By its part, there is an inversion twin with symmetry-related disorder of the oxygen/fluorine atoms in the [OTeF₅]⁻ group. This F/O disorder was expected, as there is no cation-anion interaction that can help orient the oxygen atom and overcome such disorder, as was observed in the crystal structure of [(PS)H][OTeF₅] (PS = 1,8-bis(dimethylamino)naphthalene).^[42] In our case, two different Te–F/O bond lengths are observed, i.e. 179.9(6) and 184.3(6) pm, but within the range expected for the free teflate anion, for which the Te–O bond length is 180.3 pm and the average Te–F distance is 187.0 pm.^[42] Interestingly, in the related [OSF₅]⁻ anion, the S–O and S–F bonds can be easily differentiated in the crystal structure of [Cu(NCMe)₄][OSF₅], but in this case many H–F and H–O contacts are established between the [OSF₅]⁻ anion not only with the coordinated MeCN ligands, but also with free acetonitrile molecules.^[40]

Remarkably, when certain donor solvents enter in contact at low temperature with compound [NEt₄]₂[Ni(OTeF₅)₄] (**1**), the complete substitution of the teflate ligands can be avoided. This was the case when trying to crystallize compound [NEt₄]₂[Ni(OTeF₅)₄] (**1**) by vapor diffusion of Et₂O into a solution of the compound in CH₂Cl₂ at –24 °C. In fact, the complex anion

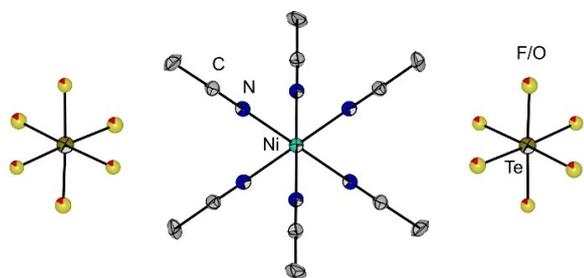


Figure 4. Molecular structure of [Ni(NCMe)₆][OTeF₅]₂ (**2**). Hydrogen atoms have been omitted for clarity. Displacement ellipsoids set at 50% probability. The F/O disorder is shown by mixed color sites. Selected bond lengths [pm] and angles [°]: Ni–N 206.2(4), N–C 112.9(6), C–C 146.1(7), Te–F/O 179.9(6)/184.3(6) (bond lengths corresponding to *trans*-standing bonds), N–Ni–N 88.75(15)/91.25(15), Ni–N–C 176.5(4), N–C–C 179.0(6), F/O–Te–F/O 95.7(4)/87.3(4)/84.2(4). For crystallographic details see Supporting Information.

is able to coordinate two molecules of diethyl ether in the axial positions of an octahedron, therefore forcing the teflate ligands into the equatorial plane, giving rise to [NEt₄]₂[*trans*-Ni(OEt₂)₂(OTeF₅)₄]-CH₂Cl₂ (**3**) (see Figure 5).

Compound **3** crystallizes in the orthorhombic space group *Pcca*. The nickel center in the [*trans*-Ni(OEt₂)₂(OTeF₅)₄]²⁻ anion shows a distorted octahedral coordination environment, where the Ni–O bonds to the Et₂O molecules coordinated in the axial positions are elongated with respect to those corresponding to the teflate ligands (204.09(16) pm (av.) vs. 208.04(16) pm (av.)). This evidences that the Et₂O ligands are more weakly coordinated to the nickel center than the teflate ligands. Additionally, it is interesting to note that the Ni–O distances in the four teflate ligands in the equatorial plane are longer than in the parent [Ni(OTeF₅)₄]²⁻ anion: 204.09(16) pm (av.) vs. 194.5(7) pm (av.) (cf. Figure 1). A similar effect is observed when comparing the Al–OTeF₅ bond lengths in [PPH₄][Al(OTeF₅)₄] (173.4(2) pm, av.)^[7] and in [Li(thf)₄][*trans*-Al(OTeF₅)₄(thf)₂] (185.1(6)–186.1(6) pm).^[43]

These results led us to envision a possible partial substitution of the teflate ligands to form heteroleptic nickel teflate complexes with ancillary ligands. With this aim, we performed the equimolar reaction of compound [NEt₄]₂[Ni(OTeF₅)₄] (**1**) with 2,2'-bipyridine (bpy) under different reaction conditions. In none of the cases could we obtain anything different than mixtures of species which could not be separated, but which included the [Ni(bpy)₃]²⁺ cation complex. This would imply again the easiness of dissociation of the weakly coordinated teflate groups, even when there is not even an excess of the introduced ligand. Similarly, when refluxing NiF₂·4H₂O with bpy

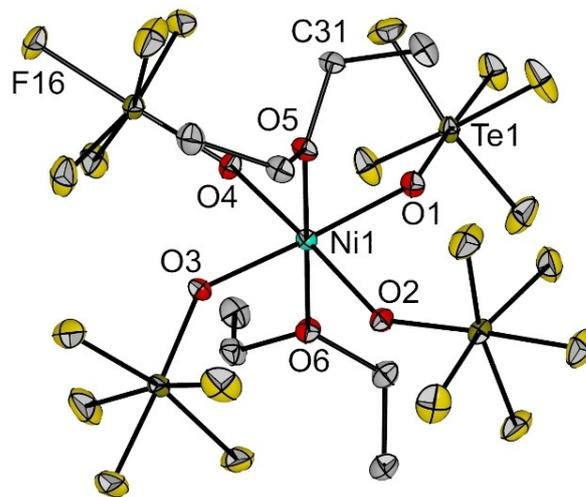


Figure 5. Molecular structure of the [*trans*-Ni(OEt₂)₂(OTeF₅)₄]²⁻ anion in the solid state as found in crystals of **3**. The [NEt₄]⁺ cations and hydrogen atoms have been omitted for clarity, as well as a co-crystallized CH₂Cl₂ molecule. Displacement ellipsoids set at 50% probability. Selected bond lengths [pm] and angles [°]: Ni1–O1 202.87(16), Ni1–O2 205.92(16), Ni1–O3 202.71(15), Ni1–O4 204.84(16), Ni1–O5 207.61(16), Ni1–O6 208.46(16), O1–Ni1–O2 90.28(6), O2–Ni1–O3 90.39(6), O3–Ni1–O4 88.97(6), O4–Ni1–O1 90.54(6), O1–Ni1–O5 89.63(6), O2–Ni1–O5 92.14(6), O3–Ni1–O5 87.43(6), O4–Ni1–O5 91.39(6), O5–Ni1–O6 179.71(6). For crystallographic details see Supporting Information.

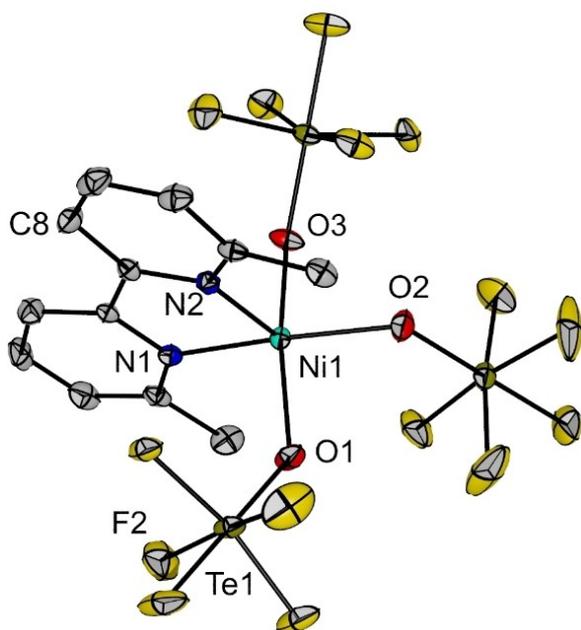
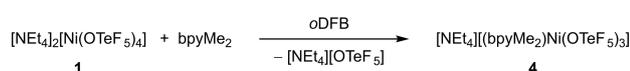


Figure 6. Molecular structure of the $[\text{Ni}(\text{bpyMe}_2)(\text{OTeF}_5)_3]^-$ anion in the solid state as found in crystals of **4**. Only one of the two independent anions found is shown. The $[\text{NEt}_4]^+$ cation and hydrogen atoms have been omitted for clarity. Displacement ellipsoids set at 50% probability. Selected bond lengths [pm] and angles [°]: Ni1–O1 201.3(4), Ni1–O2 199.7(4), Ni1–O3 206.3(4), Ni1–N1 201.5(5), Ni1–N2 202.1(4), O1–Ni1–O2 88.42(18), O1–Ni1–O3 158.33(14), O2–Ni1–O3 88.47(18), N1–Ni1–N2 82.05(17), O1–Ni1–N2 104.92(16), O2–Ni1–N2 112.48(17), O3–Ni1–N2 96.07(16). For crystallographic details see Supporting Information.

in methanol, the same cation $[\text{Ni}(\text{bpy})_3]^{2+}$ seems to be formed, whereas the fluorides act as counterions.^[44] In contrast, the reaction of the analogue fluoride species $\text{Li}_2[\text{NiF}_4]$ with an excess of pyridine (py) was reported to render crystals of the species $[\text{trans-NiF}_2(\text{py})_4]$.^[45]

Trying to overcome the easy dissociation, we decided to try the equimolar reaction of compound $[\text{NEt}_4]_2[\text{Ni}(\text{OTeF}_5)_4]$ (**1**) with 2,2'-dimethyl-6,6'-bipyridine (bpyMe₂) in oDFB. In this case, only one teflate ligand was dissociated and the coordination sphere of the Ni(II) center was extended to form compound $[\text{NEt}_4][\text{Ni}(\text{bpyMe}_2)(\text{OTeF}_5)_3]$ (**4**) selectively (Scheme 3). The methyl groups in the ancillary ligand seem to play here a key role to prevent the dissociation of further teflate ligands. The same ligand was also successful in preventing mixtures of species in the case of compound $[\text{Na}(\text{dme})_2][\text{Ni}(\text{OC}_4\text{F}_9)_4]$, but in this case two $[\text{OC}_4\text{F}_9]^-$ anions were dissociated to form the distorted tetrahedral complex $[\text{Ni}(\text{bpyMe}_2)(\text{OC}_4\text{F}_9)_2]$.^[16]

Single crystals of **4** were grown by slow vapor diffusion of *n*-pentane into a solution of compound **4** in oDFB. The species



Scheme 3. Reaction of complex **1** with bpyMe₂ to yield $[\text{NEt}_4][\text{Ni}(\text{bpyMe}_2)(\text{OTeF}_5)_3]$ (**4**).

crystallizes in the triclinic space group *P*-1 and two independent $[\text{Ni}(\text{bpyMe}_2)(\text{OTeF}_5)_3]^-$ anions are found in the asymmetric unit, which show no interaction with the cations. In Figure 6 one of the two anions is depicted. This anionic complex shows a fivefold coordinated nickel(II) center with a distorted square pyramidal structure, the structural parameter being $\tau_5 = 0.1$.^[46] The N2 atom occupies the apical position, whereas N1 and the three teflate ligands occupy the four positions of the base. Interestingly, although both Ni–N bond lengths are indistinguishable within the experimental error, the three Ni–O bonds are different, but in all cases elongated with respect to those found in the parent compound **1**.

Conclusion

The reaction of neat ClOTeF₅ with $[\text{NEt}_4]_2[\text{NiCl}_4]$ has led to the synthesis of compound $[\text{NEt}_4]_2[\text{Ni}(\text{OTeF}_5)_4]$ (**1**), which is extremely moisture sensitive, but thermally stable under inert conditions. Magnetic studies have revealed an effective magnetic moment that indicates two unpaired electrons in the nickel center, therefore accounting for its paramagnetic behavior. The $[\text{Ni}(\text{OTeF}_5)_4]^{2-}$ anion presents a distorted tetrahedral structure, unlike the polymeric $[\text{NiF}_4]^{2-}$, therefore being an analogue of this fluoronickelate, but featuring the discrete structure of the heavier halonickelates. This complex has enabled the unprecedented study of the electronic properties of the teflate group in coordination chemistry, for which values of $Dq = 461 \text{ cm}^{-1}$ and $B = 896 \text{ cm}^{-1}$ were derived from its UV-Vis-near-IR spectrum. These parameters, together with the value of the effective magnetic moment, demonstrate that the $[\text{OTeF}_5]^-$ is a weak/medium-field ligand, similarly to the fluoride. According to the Te–O vibration at 834 cm^{-1} , it could be concluded that the Ni–O bonds in the $[\text{Ni}(\text{OTeF}_5)_4]^{2-}$ anion have an ionic character. In fact, they are easily dissociated when the complex is dissolved in a donor solvent, as was proved by the formation of $[\text{Ni}(\text{NCMe})_6][\text{OTeF}_5]_2$ (**2**) in an acetonitrile solution. By slow gas diffusion of Et₂O into a CH₂Cl₂ solution of **1**, dissociation of the teflate ligands can be prevented and two Et₂O molecules coordinate in the axial positions of a distorted octahedron, whereas the teflate ligands are pushed into the equatorial plane resulting in $[\text{NEt}_4]_2[\text{trans-Ni}(\text{OEt}_2)_2(\text{OTeF}_5)_4] \cdot \text{CH}_2\text{Cl}_2$ (**3**). Unlike the unselective reaction of compound **1** with bpy, the reaction with the related bpyMe₂ ligand yields the five-coordinate $[\text{NEt}_4][\text{Ni}(\text{bpyMe}_2)(\text{OTeF}_5)_3]$ species (**4**), in which only one teflate ligand has been displaced. The challenging chemistry of Ni(II) teflate species can now be better understood and paves the way to unveiling the viability of the $[\text{OTeF}_5]^-$ ligand to also stabilize the high oxidation state +IV of nickel. Additionally, the ligand-field properties of the pentafluorothellurate group have been clarified and therefore the study of the magnetic and structural properties of different teflate coordination complexes can be tackled from a new perspective.

Experimental Section

General procedures and materials

All experiments were performed under rigorous exclusion of moisture and oxygen using standard Schlenk techniques. Solids were handled in a MBRAUN UNILab plus glovebox under an argon atmosphere ($O_2 < 0.5$ ppm, $H_2O < 0.5$ ppm). Solvents were dried using a MBraun SPS-800 solvent system (CH_2Cl_2 , CH_3CN , *n*-pentane), or with CaH_2 (oDFB, Et_2O , CD_3CN) before use and stored over 3 or 4 Å molecular sieves. $[NEt_4]_2[NiCl_4]^{[47]}$ and $ClOTeF_5^{[19b]}$ were prepared as described elsewhere. 2,2'-dimethyl-6,6'-bipyridine (bpyMe₂) was dried at 120 °C under dynamic vacuum before use. All other reagents were purchased from standard commercial suppliers and used as received. Elemental analyses (CHNS) were carried out using a VARIO EL elemental analyzer. IR spectra were measured on neat solid samples at room temperature inside a glovebox under an argon atmosphere using a Bruker ALPHA FTIR spectrometer with a diamond ATR attachment with 32 scans and a resolution of 4 cm^{-1} . NMR spectra were recorded on a JEOL 400 MHz ECS spectrometer. Crystal data were collected with MoK α radiation on a Bruker D8 Venture diffractometer with a CMOS area detector. Single crystals were picked at -40 °C under nitrogen atmosphere and mounted on a 0.15 mm Mitegen micromount using perfluoroether oil. The structures were solved with the ShelXT^[48] structure solution program using intrinsic phasing and refined with the ShelXL^[49] refinement package using least squares minimizations by using OLEX2.^[50] The program Diamond V4.6.4 was used for visualization.^[51] Crystal data and other details of the structure analyses are summarized in Tables S1–S4. Suitable crystals for X-ray diffraction studies were obtained as indicated in the corresponding experimental entry.

Synthesis of $[NEt_4]_2[Ni(OTeF_5)_4]$ (1)

$[NEt_4]_2[NiCl_4]$ (100 mg, 217 μ mol, 1 equiv.) was weighed into a Schlenk flask with a greaseless Teflon stopcock. After cooling down to -196 °C, $ClOTeF_5$ (357 mg, 1.30 mmol, 6 equiv.) condensed onto it. The mixture was allowed to warm to room temperature under stirring, resulting in a brownish slurry, whereas evolution of a yellow gas was observed. The gas was identified as Cl_2 by gas-phase UV-vis spectroscopy (see Figure S1). After 30 minutes of stirring, all volatiles were removed under vacuum. After drying overnight under vacuum a deep blue solid was obtained and identified as compound **1** (275 mg, 216 μ mol, quant.). IR (ATR, 298 K, Figure S3): $\tilde{\nu}/cm^{-1} = 3001$ (w), 1486 (w), 1459 (w), 1443 (w), 1397 (w), 1368 (w), 1186 (w), 1173 (w), 1069 (w), 1054 (w), 1032 (w), 834 (m, Te–O), 783 (m), 662 (vs, Te–F), 614 (w), 445 (m, Ni–O). **Elemental analysis** calcd (%) for $C_{16}H_{40}F_{20}N_2NiO_4Te_4$: C 15.1, H 3.2, N 2.2; found: C 15.4, H 3.2, N 2.2. **UV-Vis** (CH_2Cl_2 , Figure 3): $\lambda_{max}/nm = 573, 630, 766, 1175$.

Crystal growth of $[NEt_4]_2[Ni(OTeF_5)_4]$ (1)

Single crystals of **1** suitable for X-ray diffraction were obtained by slow evaporation of a solution of the compound in oDFB (ca. 20 mg in 1 mL). This solution was placed in a Y-shaped schlenk tube with a greaseless Teflon stopcock, and the empty side arm was placed in a cooling bath, which was cooled from room temperature to 0 °C along 15 h, controlled by a cryostat. Blue single crystals of $[NEt_4]_2[Ni(OTeF_5)_4]$ (**1**) were obtained.

Synthesis and crystal growth of $[Ni(NCMe)_6][OTeF_5]_2$ (2)

$[NEt_4]_2[Ni(OTeF_5)_4]$ (30 mg, 23.6 μ mol) was dissolved in 1 mL MeCN in a Y-shaped schlenk tube with a greaseless Teflon stopcock. In the side arm, 2 mL Et_2O were added. After storing the tube at -24 °C for some days, pale purple single crystals suitable for X-ray diffraction were obtained. Additionally, the supernatant solution could be removed with a syringe and after washing with Et_2O (2 \times 1 mL) and drying shortly under vacuum, compound **2** could be obtained as purple crystals (17 mg, 21.7 μ mol, 92% yield). IR (ATR, 298 K, Figure S4): $\tilde{\nu}/cm^{-1} = 3000$ (w), 2943 (w), 2326 (w, $\nu_3 + \nu_4$), 2299 (m, ν_2 : C \equiv N), 1419 (w), 1375 (w), 1039 (w), 944 (w), 865 (s, Te–O), 813 (m), 685 (m), 665 (m), 630 (vs, Te–F), 578 (w), 463 (w), 409 (m).

Crystal growth of $[NEt_4]_2[trans-Ni(OEt)_2(OTeF_5)_4] \cdot CH_2Cl_2$ (3)

$[NEt_4]_2[Ni(OTeF_5)_4]$ (10 mg, 7.9 μ mol) was dissolved in 0.5 mL CH_2Cl_2 in a Y-shaped schlenk tube with a greaseless Teflon stopcock. In the side arm, 1 mL Et_2O was added. After storing the tube at -24 °C for some days, orange single crystals suitable for X-ray diffraction were obtained.

Synthesis of $[NEt_4][Ni(bpyMe_2)(OTeF_5)_3]$ (4)

A mixture of $[NEt_4]_2[Ni(OTeF_5)_4]$ (50 mg, 39.3 μ mol, 1 equiv.) and bpyMe₂ (7.2 mg, 39.3 μ mol, 1 equiv.) was dissolved in oDFB (1 mL). The mixture turned green while undissolved material disappeared progressively. After stirring for 5 min, the solvent was evaporated until there was ca. 0.5 mL left. *n*-pentane (0.5 mL) was added and a pale yellow-green solid precipitated. The solvent was filtered off, and the resulting solid dried under vacuum. Some $[NEt_4][OTeF_5]$ still remained in the sample. Keeping a solution of the obtained mixture in oDFB or CH_2Cl_2 (1 mL) at -24 °C for some days did not enable to completely remove it to obtain **4** as a pure substance. IR of the obtained solid material (ATR, 298 K, Figure S5): $\tilde{\nu}/cm^{-1} = 3000$ (w), 1606 (w), 1574 (w), 1486 (m), 1474 (m), 1457 (m), 1443 (w), 1396 (w), 1368 (w), 1309 (w), 1262 (w), 1249 (w), 1183 (m), 1175 (w), 1132 (w), 1031 (w), 1025 (w), 1001 (w), 864 (m, Te–O, $[OTeF_5]^-$), 852 (s, Te–O), 845 (m), 792 (m), 784 (m), 656 (vs, Te–F), 634 (vs, Te–F, $[OTeF_5]^-$), 598 (m), 574 (w).

Crystal growth of $[NEt_4][Ni(bpyMe_2)(OTeF_5)_3]$ (4)

The mixture of $[NEt_4][Ni(bpyMe_2)(OTeF_5)_3]$ and $[NEt_4][OTeF_5]$ prepared as described previously was dissolved in 1 mL oDFB in a Y-shaped schlenk tube with a greaseless Teflon stopcock. In the side arm, 1.5 mL *n*-pentane were added. After storing the tube at -24 °C for some days, yellow single crystals suitable for X-ray diffraction were obtained.

Deposition Numbers 2171818 (for **1**), 2172253 (for **2**), 2172098 (for **3**), 2172131 (for **4**) 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.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: coordination chemistry · fluorine chemistry · ligand field theory · nickel · pentafluoroorthotellurate

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