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A Simple Route to Single-Scorpionate Nickel(II) Complexes with Minimum Steric Requirements

Patrick J. Desrochers,* Adam L. Corken, Richard M. Tarkka,* Brian M. Besel, Erin E. Mangum, and Tiffany N. Linz

Department of Chemistry, University of Central Arkansas, Conway, Arkansas 72035

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Single-scorpionates of nickel(II), Tp^RNiX or Tpm^RNiX, are kinetic products whose preparation has generally required considerable steric constraints on the ligands (i.e., R = phenyl, *tert*-butyl, or isopropyl) to prevent formation of intractable two-ligand products like $(Tp^R)_2Ni$. It is well established that the facial tridentate chelates hydrotris(3,5-dimethylpyrazolyl)borate (Tp^{*-}), tris(3,5-dimethylpyrazolyl)methane (Tpm*), and trispyrazolylmethane (Tpm), all readily form two-ligand complexes as thermodynamic products. For the first time we report a route to the single-ligand complex $TpmNiX_2(OH_2)_n$ (X = Cl and Br). We also report a novel method for making single-ligand nickel(II) scorpionate complexes using preformed tetrahalonickelate(II) ion in nitromethane. The complex $Tpm^*NiCl_2(OH_2)_n$ was also prepared here for the first time utilizing an alternative method first reported by Zargarian and co-workers (*Inorg. Chim. Acta* **2006**, 2592). $TpmNiX_2(OH_2)_n$ are kinetic products, and although they are stable indefinitely in the solid state, they readily convert to the thermodynamic product $(Tpm)_2Ni^{2+}$ in solution over the course of several hours at room temperature and in a matter of minutes at 100 °C. The new nitromethane/NiX_4^{2-} method offers an alternative route to monoscorpionates of first row transition metals, for which tetrahalometallate ions are common. $HOCH_2Tpm$ (2,2,2-tris(pyrazolyl)ethanol) was covalently attached to polystyrene synthesis beads and found to bind nickel(II) (from NiX_4^{2-}) in a manner similar to Tpm. Solid state electronic spectra of supported-$TpmNiCl_2$ are comparable to those measured for their homogeneous complexes. Covalently supported scorpionates are expected to further extend the utility of this rich ligand class in areas of heterogeneous catalysis and metal-protein interactions.

Introduction

Scorpionates, first engineered by Trofimenko, are firmly established ligands in the field of coordination chemistry.[1] Their widespread utility stems from versatile steric and electronic properties that can be controlled through alterations in their pyrazole ring substituents (Figure 1). Our recent studies have shown that single-ligand Tp^*NiNO_3 reacts selectively with cysteine (Cys) at the N-terminus of an oligopeptide chain.[2] Cys in other positions did not bind, nor did other amino acids at the N-terminus of the chain. In the course of investigating the potential of this selective binding as the basis for a cysteine indicator, we wanted to covalently immobilize a scorpionate onto a solid support and show that the supported scorpionate possessed similar reactivity to the solution-phase analogues. Covalently immobilized scorpionates to date have been limited to mixed N,N,O-donor ligands with a pyrazolylmethane linkage attached to Merrifield resin.[3] Immobilization of traditional N,N,N-donor Tp^R scorpionates has involved only physisorbed species on solid substrates.[4] Our decision to investigate covalently immobilized Tpm (Scheme 1) was motivated by Reger's success in attaching multiple functionalized Tpm ligands[5] to organic cores for the construction of supramolecular coordination polymers.[6]

* To whom correspondence should be addressed. E-mail: patrickd@uca.edu (P.J.D.), rtarkka@uca.edu (R.M.T.).

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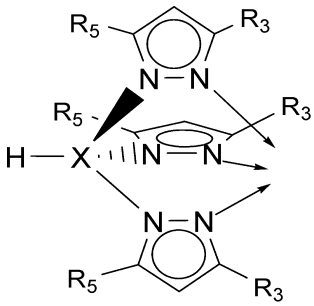
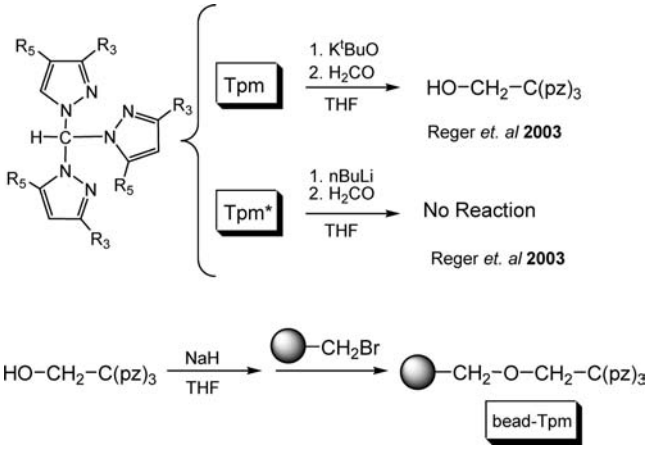


ligand	X	R_5	R_3
Tpm	C	H	H
$Tp^{\ominus}$	B	H	H
Tpm*	C	CH_3	CH_3
$Tp^{*\ominus}$	B	CH_3	CH_3

Figure 1. Scorpionate ligand abbreviations.

Scheme 1



Because the known nickel(II) complexes of Tpm are exclusively two-ligand products,[7] comparison between immobilized Tpm and solution-phase analogues necessitated the development of a reliable synthetic route to single-ligand TpmNi complexes. To date, there are only two previous reports of Tpm^R derivatives forming single-ligand products with nickel. Zargarian and co-workers obtained one-ligand Tpm*Ni(κ^1-NO_3)(κ^2-NO_3) when they reacted Tpm* with nickel(II) nitrate in acetone.[8] Unfortunately, that method does not work with Tpm (*vide infra*): two-ligand product is produced. We were thus precluded from using Zargarian's method because our immobilized Tpm (Scheme 1) necessarily lacks methyl groups in the 3 and 5 positions. The method used to attach the -CH_2OH synthetic handle to Tpm does not work with Tpm* (Scheme 1).[9] Another single-ligand product, O_3STpm^RNiCl, was reported by Kläui and co-workers.[10] Sterically encumbered ^{t}Bu-pyrazolyl rings were used, allowing the complex to be prepared *via* the direct reaction of the ligand-thallium(I) complex and nickel(II) chloride. Herein we report a simple, direct route to single-scorpionate nickel halides that works with both Tpm^R and Tp^R classes of ligands. Immobilized Tpm is shown to form single-ligand nickel complexes in a manner analogous to its solution-phase counterpart.

Experimental Section

All reagents and solvents were purchased from Fisher or Sigma-Aldrich and were used as received except where noted. Novasyn TG Bromo resin was obtained from Novabiochem and had a functional group density of 0.30 mmol/g of bead. Reger's methods were used to prepare tris(3,5-dimethyl-1-pyrazolyl)methane (Tpm*)[5] and 2,2,2-tris(pyrazolyl)ethanol, ($HOCH_2C(pz)_3$; $HOCH_2$-Tpm).[9] Elemental analyses were performed by Atlantic Microlab of Norcross, GA.

Spectroscopy and Magnetic Measurements. ^{1}H and ^{13}C NMR were recorded using a JEOL ECX 300 FT instrument. Infrared spectra were recorded using a Thermo Nicolet FT IR 100 spectrometer. Electronic spectra were recorded using Varian Cary 50 instruments with 1 cm quartz cells, for solution phase measurements, and a video Barrelino diffuse reflection probe (Harrick Scientific) interfaced to the spectrometer *via* a fiber optic coupler for solid phase samples. Solid samples for UV−visible spectroscopy were sandwiched between microscope slides. Magnesium oxide powder suspended in like manner was used for a background blank.

Tris(pyrazolyl)methane (Tpm). Tpm was prepared according to Reger's method.[5] In our hands, the crude Tpm was not pure enough for use in subsequent reactions. It was thus recrystallized from water, using activated carbon to remove colored impurities. The resultant white needles were taken up in dichloromethane for drying: phase-separated water was removed by pipet, after which the solution was dried over anhydrous sodium sulfate. The Na_2SO_4 was then removed by gravity filtration. Rotary evaporation of the dichloromethane left pure Tpm as determined by ^{1}H and ^{13}C NMR spectroscopy and melting point, 103−104 °C (Lit 105−106 °C).[11]

Synthesis of $TpmNiCl_2(OH_2)_3$. This complex was prepared by the direct reaction of Tpm with tetrachloronickelate(II) prepared *in situ*. Solid nickel(II) chloride hexahydrate (504 mg, 2.12 mmol) was dehydrated in a 50 mL flask under vacuum. To the orange anhydrous nickel(II) chloride was added 25 mL of nitromethane, and the mixture was vigorously stirred. Solid tetrabutylammonium chloride hydrate (2.36 g, 8.43 mmol) was then added to the nickel chloride slurry along with an additional 10 mL of nitromethane, whereupon the mixture immediately yielded the characteristic teal blue color of the $NiCl_4^{2-}$ ion (identity confirmed by electronic spectroscopy).[12] Stirring of the mixture for an additional 20 min completed the dissolution of the remaining nickel chloride, giving a clear deep teal blue solution. To this mixture was added dropwise a solution of Tpm (472 mg, 2.12 mmol) dissolved in 4 mL of nitromethane. The crude product precipitated almost immediately from this mixture as a light blue powder. Thin layer chromatography (20:80 methanol/chloroform; 70−230 mesh, 60 Å silica gel) indicated the major impurity to be residual $[NBu_4]Cl$. The product was purified by first dissolving in water, after which the dropwise

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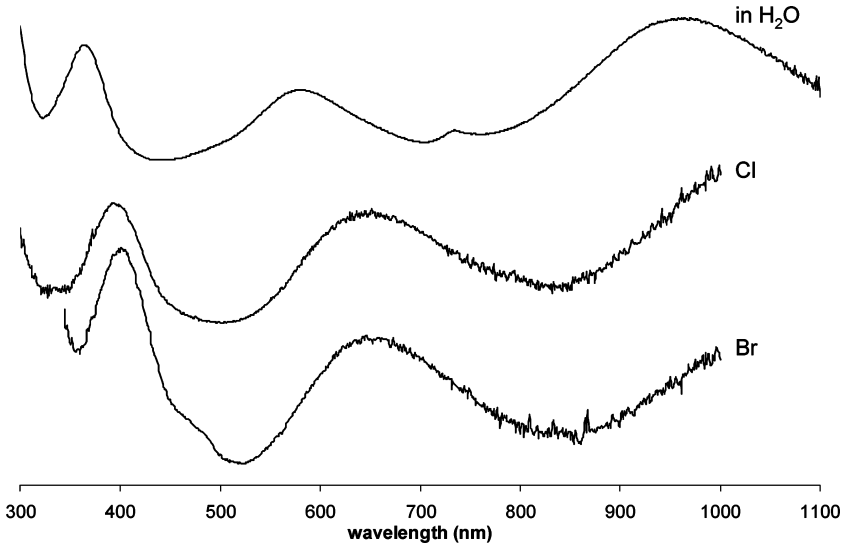

Figure 2. Electronic spectra of $TpmNiX_2(OH_2)_n$ in the solid state (by diffuse reflectance, bottom two traces) and dissolved in water (top trace). The bottom two traces are for solid $TpmNiCl_2(OH_2)_3$ and solid $TpmNiBr_2(OH_2)_{2.5}$. The top spectrum is an aqueous solution of $TpmNiCl_2(OH_2)_3$; the same aqueous spectrum results when the bromide is used.

Table 1. Electronic Transition Energies (cm^{-1}) for Single-Tpm^R Complexes of Nickel(II) in Different Phases

	phase	$^3T_1(P)\leftarrow{}^3A_2$	$^3T_1(F)\leftarrow{}^3A_2$	$^1E\leftarrow{}^3A_2$	$^3T_2\leftarrow{}^3A_2$
$TpmNiCl_2(OH_2)_3$	(s)[a]	25,580	15,530		<10,000
$TpmNiBr_2(OH_2)_{2.5}$	(s)[a]	25,190	15,480		<10,000
$Tpm^*NiCl_2(OH_2)_{1.5}$	(s)[a]	24,810	15,270		<10,000
$Tpm^*NiCl_2(OH_2)_{1.5}$	(aq)[b]	27,400 (14)[c]	16,950 (5)	13,700 (2)	10,340 (10)
$TpmNiCl_2(OH_2)_3$	(aq)[b]	27,700 (7)	17,390 (4)	13,700 (2)	10,440 (9)

[a] Diffuse reflectance; lower limit of 10,000 cm^{-1}. [b] The aqueous species in both cases is postulated to be $Tpm^RNi(OH_2)_3^{2+}$. [c] ε in parentheses (M^{-1} cm^{-1}).

addition of concentrated hydrochloric acid re-precipitated the product as an analytically pure pale blue solid. The solid was washed sequentially with nitromethane and diethyl ether, and air-dried. Yield 400 mg (48%). Anal. Expt (theory): C, 30.32 (30.19); H, 4.06 (4.05); N, 21.21 (21.12). IR, cm^{-1} (KBr): 3422 s, 3126 s, 2968 m, 1637 m, 1518 m, 1442 m, 1410 m, 1286s, 1250 m, 1092 m, 1055 m, 983 m, 859 m, 791 s, 767 s, 608 m (see also Supporting Information, Figure S1). UV−vis spectra results are summarized in Figure 2 and Table 1.

Synthesis of $TpmNiBr_2(OH_2)_{2.5}$. This product was prepared from the reaction of $NiBr_4^{2-}$ (*in situ*) and Tpm following the method described above for the chloride analogue. As with chloride, this product is readily purified from aqueous solution using concentrated hydrobromic acid. Yield 600 mg (60%). Anal. Expt (theory): C, 25.12 (25.14); H, 3.10 (3.17); N, 17.55 (17.55). IR, cm^{-1} (KBr): 3434 s, 3120 s, 2964 m, 1655 m, 1516 m, 1442 m, 1400 m, 1286 s, 1249 m, 1092 m, 1054 m, 982 m, 859 m, 792 s, 766 s, 608 m (see also Supporting Information, Figure S1). UV−vis spectra results are summarized in Figure 2 and Table 1.

Synthesis of $Tpm^*NiCl_2(OH_2)_{1.75}$. This solid was prepared using the method reported for the preparation of $Tpm^*Ni(\eta^1\text{-}NO_3)(\eta^2\text{-}NO_3)$.[8] Specifically, solid nickel(II) chloride hexahydrate (25 mg, 0.11 mmol) was added to a solution of Tpm* (39 mg, 0.13 mmol) in 10 mL of acetone. This mixture was vigorously stirred for several hours; gradual dissolution of the nickel chloride led to the formation of a pale green solid that precipitated from the reaction mixture. This solid was filtered, washed with acetone and air-dried. The solid was washed with several portions of chloroform to remove unreacted Tpm* and washed with diethyl ether giving the product as a pale green powder. Yield 30 mg (50%). Anal. Expt (theory): C, 41.87 (41.81); H, 5.42 (5.60); N, 18.35 (18.29). IR, cm^{-1} (KBr): 3357 s, 3095 w, 2982 w, 2922 m, 1666 m, 1570 s, 1466 s, 1410 s, 1396 s, 1308 s,1269 s, 1161 w, 1113 w, 1045 m, 982 w, 916 m, 864 s, 812 w s, 791 m, 706 s (see also Supporting Information, Figure S1). UV−vis spectra results are summarized in Supporting Information, Figure S2 and Table 1.

Bead-Tpm. Novasyn TG Bromo resin (300 mg, 0.090 mmol) was swelled in dry DMF for 30 min. The beads were drained and washed with additional DMF before use. In a separate 10 mL Schlenk tube, $HOCH_2$-Tpm (116 mg, 0.475 mmol, 5.3 equiv relative to the Br functional group density on the beads) was dissolved in 1.5 mL of DMF. NaH (19 mg of 60% dispersion in mineral oil, 1.0 equiv relative to $HOCH_2$-Tpm) was added, and the mixture was stirred under a blanket of argon at room temperature. After 20 min, the salt solution was transferred via cannula to the 25 mL Schlenk tube containing the swelled beads. The mixture was heated to 90 °C for 5 h, *without stirring*, under a blanket of argon. The flask was rocked by hand every 15−20 min to agitate the suspension. The suspension was filtered on a small glass frit, washed thoroughly with DMF, then CH_2Cl_2. The beads were dried with a slow stream of argon. ^{13}C NMR ($CDCl_3$): 141.3, 131.1, 106.6, 89.7 ppm (Supporting Information, Figure S3). Note that PEG chains, located between the core of the beads and the functional groups, enable NMR spectra to be obtained under normal conditions.

Metalation of Bead-Tpm. Metalation of Bead-Tpm was accomplished with nickel by passing a 0.1 M solution of $NiCl_4^{2-}$ (prepared as described above) in nitromethane down a packed column of beads resting in a vial fitted with a sintered glass frit. On contact with this solution, the previously pale amber beads developed a distinct green color, indicating nickel(II) coordination. Residual nickel solution was thoroughly washed from the beads with additional nitromethane until the filtrate was colorless. After washing the beads with diethyl ether and drying them under a nitrogen stream, the color persisted. The electronic spectrum of this bead-$TpmNiCl_2$ species was recorded by diffuse reflectance. Unmetallated beads were used for the background correction. As a

control, a sample of Novasyn TG Bromo resin, which lacks the Tpm group, was subjected to the same procedure. After exposure to $NiCl_4^{2-}$/nitromethane and subsequent washing, there was no color change, indicating that the binding that leads to the color change when bead-Tpm is treated with $NiCl_4^{2-}$ is caused by nickel interacting with Tpm and not with the poly(ethyleneglycol) tethers.

Results and Discussion

The strong affinity of tris(pyrazolyl)borates ($Tp^{R\ -}$) and tris(pyrazolyl)methanes (Tpm^R) for first row transition metals leads them to frequently form coordinatively saturated complexes with the general structure $(Tp^R)_2M$ (two-ligand products). The unreactive nature of the thermodynamic two-ligand products precludes their use in catalysis or bioinorganic modeling. Instead, it is the single-ligand products, of the form Tp^RMX and Tpm^RMX_2, respectively, that serve as catalysts[13,14] and have provided the wealth of knowledge in modeling metalloprotein active sites.[15] Extending this utility to immobilized scorpionates motivated the present work.

The preparation of single-ligand metal-scorpionates requires some method of inhibiting the formation of two-ligand products. When the 3-position of the pyrazole rings are substituted with sterically bulky groups (*t*-butyl, isopropyl, neopentyl, phenyl, mesityl, Figure 1), the two-ligand products are thermodynamically unstable. In such cases, potassium or sodium salts of these ligands or thallium(I)-scorpionate precursors can be reacted directly with simple metal salts, yielding single ligand products free of two-ligand contaminants.[1,16] When methyl groups substitute for 3-H positions on the pyrazole rings (i.e., Tp*), the relative energy of the methyl two-ligand product is destabilized enough to make the kinetic barrier to its formation relatively high. However, the reaction conditions to prepare single-Tp* products must be chosen carefully because the two-ligand complex remains the thermodynamically preferred end-product.

These methods are not, however, without some drawbacks. Unless the substituents on the 3 and 5 positions of the pyrazole ring are identical, the synthesis of the Tp^R and Tpm^R scorpionates from them can be plagued by the formation of multiple positional isomers.[5,17] Other complications that can arise from the bulky substitutents include 1,2-borotropic shifts and the formation of unreactive dimers.[17c] The toxicity of thallium also motivates chemists to seek alternatives to its use as a synthetic precursor wherever possible.

Tp* is the least sterically encumbered scorpionate for which single-ligand nickel(II) complexes are routinely prepared. Complexes having the form Tp*NiX (for example, Tp*NiCl,[14] Tp*Ni(κ^2-NO_3),[18,19] and Tp*Ni(κ^2-O_2CCH_3))[19] can all be made using the direct reaction of the corresponding nickel(II) halide, nitrate, or acetate with KTp*. The chelating ability of nitrate and acetate anions and the addition of the ligand precursor slowly to an excess of NiX_2 were credited with providing sufficient kinetic control to retard formation of the two-ligand product, Tp^*_2Ni.[19] To date, single-ligand nickel(II) complexed have not been reported for either Tp or Tpm where the pyrazole rings provide no effective steric impediment.

Once the single-Tp* products are isolated and purified, they display significant kinetic stability when used for subsequent reactions, and formation of two-ligand products is often suppressed. This has been demonstrated repeatedly in our laboratory: we routinely dissolve Tp*NiX (X = Cl, Br, and I) in donor solvents, whereupon the original four-coordinate electronic spectra change to solvent-dependent spectra characteristic of six-coordinate nickel(II). Despite this inner-sphere association of basic solvents with the Tp^*Ni^+ Lewis acid center, removal of solvent returns the complex to its original four-coordinate Tp*NiX geometry.

On the basis of this experience with Tp*NiX, it appeared that reduced solvent basicity and ancillary ligands on nickel(II) could provide sufficient kinetic control to enable the isolation of single-ligand products of the ligand Tpm. Single-Tpm complexes for other first row metals are known. For example $TpmCu(SCN)_2$ has been structurally characterized, but its synthesis resulted from the slow diffusion of Tpm into a mixture of copper(II) and thiocyanate over the course of several weeks,[20] and not from the direct, rapid addition of Tpm to the metal ion as we report here for nickel(II).

Nitromethane was chosen for the solvent of this synthesis because, despite its high polarity, it is a poor Lewis base. Tetrahalonickelate precursors were chosen because the use of related $PdCl_4^{2-}$ was a proven strategy for preparing single-

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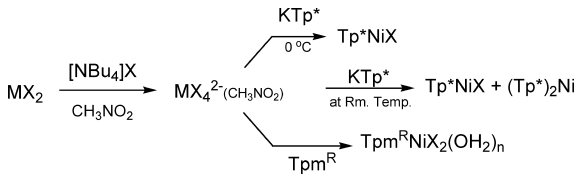
Scheme 2



scorpionates of palladium(II).[21] Electronic effects of heavier d^8 congeners dictate ligand coordination modes in their scorpionates. Often these tridentate chelates bind these metal ions in a κ^2 fashion,[22] yielding square planar MN_4 coordination spheres, where the identical nickel(II) complex has the same ligands bound in κ^3 coordination. Instances of κ^2-scorpionate coordination are rare for nickel(II).[23] It was hoped that the anionic tetrahedral NiX_4^{2-} metal center would sufficiently retard ligand substitution, enabling a single-ligand complex to form (Scheme 2). The present results demonstrate that kinetically stable single-ligand Tpm complexes of nickel will form if these products are approached along a reaction coordinate defined by minimum solvent interference and an initially crowded metal center.

When nickel(II) was complexed by a single Tpm ligand, six-coordinate geometries resulted regardless of whether the complex was made from $NiCl_4^{2-}$ or $NiBr_4^{2-}$. The familiar pattern of three spin-allowed transitions arising from a $^3A_2$ ground state (Table 1 and Figure 2) is evident in the electronic spectra for these complexes. This behavior contrasts with nickel(II)/Tp*$^-$ interactions under the same conditions (*vide infra*). Elemental analyses confirm a Tpm/Ni/X stoichiometry of 1:1:2, with residual water molecules also present. The variable water composition affects the hydrogen content measured for these solids; however, the carbon/nitrogen ratio for all of the new compounds agree with the theoretical amounts predicted for Tpm and Tpm*. A comparison of the electronic spectra for $TpmNiCl_2(OH_2)_3$ and $TpmNiBr_2(OH_2)_{2.5}$ shows a definite halide dependence, with the chloro complex exhibiting slightly higher energy transitions than the bromo form. This result is in agreement with the spectrochemical ordering of Cl > Br.

When these complexes are dissolved in water, an obvious color change ensues, and irrespective of the original halide present, the same spectrum of a six-coordinate complex results. The octahedral splitting parameter, $\Delta_o = 10{,}440\ cm^{-1}$ for aqueous $TpmNiX_2$ falls between the extremes of about $\Delta_o = 12{,}000\ cm^{-1}$ for $[Tpm_2Ni^{2+}]$[24] and $\Delta_o = 8{,}500\ cm^{-1}$ for $[Ni(OH_2)_6^{2+}]$.[12] The resultant species in water is therefore presumed to be $TpmNi(OH_2)_3^{2+}$ possessing a NiN_3O_3 coordination sphere (Figure 3). These results suggest that at least one of the two halogen ligands is bonded to the inner sphere of nickel in the solid state. In support of this conclusion is the fact that the electronic transition energies for this species in water are higher than either for the original chloro or bromo forms (as solids), in agreement with the spectrochemical ligand order OH_2 > Cl > Br.

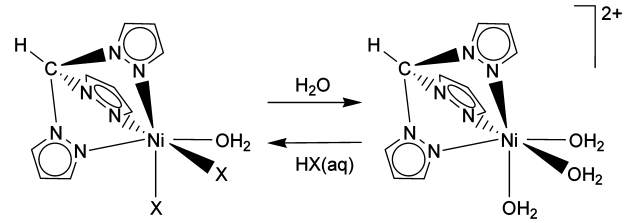
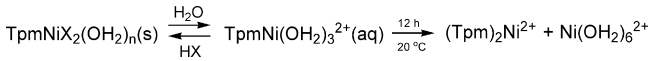


Figure 3. Water/halogen exchange in $TpmNiX_2(OH_2)$ complexes demonstrating ligand exchange on the $TpmNi^{2+}$ manifold in aqueous media.

Scheme 3



The kinetic stability of $TpmNiX_2(OH_2)_n$ is illustrated both in the way that these complexes are isolated as solids from their initial reaction mixture and in their reactive behavior when they are subsequently redissolved in aqueous solution. The poor solubility of these compounds in the initial nitromethane reaction medium allows them to be efficiently removed from the reaction as they form, trapping them in the potential energy well defined by the $TpmNiX_2(OH_2)_n$ single-ligand product. As described above, these inner sphere halides are readily replaced by aquo ligands when these solids are dissolved in water (Scheme 3 and Figure 3). This change initiates their eventual conversion to the two-ligand $(Tpm)_2Ni^{2+}$ product by a process that is completed in a matter of minutes at 100 °C or over the course of many hours at room temperature (Figure 4). While Tpm^*NiCl_2 shows the same tendency to lose inner sphere chloro ligands in water (Table 1 and Supporting Information, Figure S2), the $Tpm^*Ni(OH_2)_3^{2+}$ species formed under these conditions persists even after heating its aqueous solution for 2 h at 100 °C. The slowness of the conversion to $(Tpm)_2Ni^{2+}$ at room temperature enables the blue complex ion, $TpmNi(OH_2)_3^{2+}$, to precipitate as $TpmNiX_2(OH_2)_n$ if concentrated haloacids are introduced. This provided a means for their purification (Scheme 3).

Given the success of the NiX_4^{2-}/nitromethane method for forming single-Tpm products, it was important to see if this method could be generally employed with other scorpionates. The addition of a nitromethane solution of KTp* to deep blue $NiCl_4^{2-}$ in nitromethane led to the immediate formation of a bright pink precipitate. This solid was washed with nitromethane and ether, and Tp*NiCl was identified in the solid state by UV−vis and infrared spectroscopies.[25] Infrared spectra (Supporting Information, Figure S4) showed two bands in the 2500−2550 cm^{-1} region where characteristic scorpionate ν(B−H) vibrations are found. While the peak for the single-

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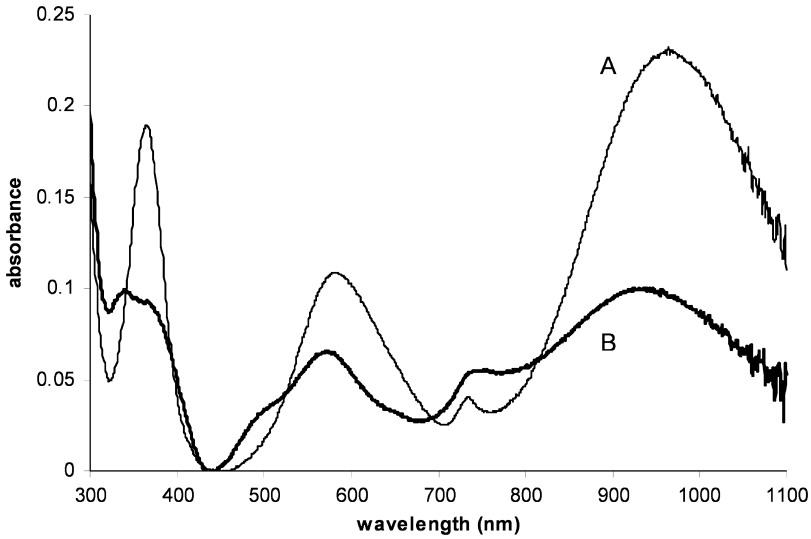

Figure 4. Electronic spectrum of $TpmNiCl_2(OH_2)_3$ in water (A), 32 mM, initially at room temperature. B is for this same solution after heating at 100 °C for 3 min and recorded at room temperature. These data summarize the spectral changes for the reaction: $2TpmNi(OH_2)_3^{2+} \rightarrow (Tpm)_2Ni^{2+} + Ni(OH_2)_6^{2+}$. The same changes occur at room temperature but over the course of about 12 h.

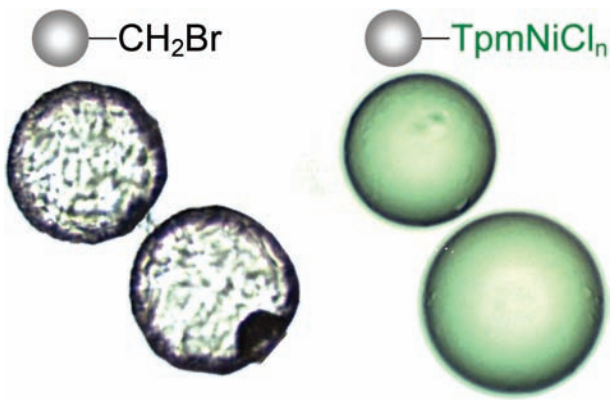

Figure 5. Photographs of magnified synthesis beads treated with nickel(II). Left, control beads, lacking covalently linked Tpm. Right, bead-Tpm following treatment with with $NiCl_4^{2-}$ and washing.

ligand product occurs at 2536 cm^{-1}, a second peak at 2510 cm^{-1} is consistent with the presence of some two-ligand product, Tp^*_2Ni. It was found that running the reaction on an ice bath and allowing the reaction mixture to slowly warm to room temperature was sufficient to entirely suppress the formation of the two-ligand product. The same procedure was used to prepare Tp*NiBr; however, the two-ligand complex begins to form in the mixture even at ice temperature, reflecting a weaker, more reactive nickel−bromine bond.

The effect of solvent and counteranion in controlling the formation of single-Tpm^R nickel(II) complexes was evident in a report by Zargarian's group where the use of nickel(II) chloride and butanol resulted in the complex salt, $[(Tpm^*)_2Ni][NiCl_4]$, possessing the two-ligand product ion.[26] While the elemental compositions of our $(Tpm^R)NiX_2(H_2O)_n$ complexes are also consistent with $[(Tpm^R_2)Ni][NiCl_4]\cdot nH_2O$, electronic spectral data support our formulation. The single crystal XRD structure of $[(Tpm^*)_2Ni][NiCl_4]$ established the presence of two distinct nickel(II) complex ions in this compound.[26] This formulation was independently supported by the UV−visible spectrum for this compound in acetonitrile: 575 nm ($\varepsilon = 102\ M^{-1}\ cm^{-1}$), 618 (152), 658 (135), 701 (127), 892 (55).[26] This electronic spectrum results from the superposition of two independent nickel(II) chromophores, $NiCl_4$ (T_d) and NiN_6 (O_h). The $NiCl_4^{2-}$ electronic spectrum is dominated by an intense envelope of transitions ($\varepsilon \sim 160$) ranging from 760−660 nm,[12] essentially coincident with the reported spectral features for $[(Tpm^*)_2Ni][NiCl_4]$. Non-centrosymmetric T_d nickel(II) complexes generally have molar absorptivities ($\varepsilon = 100-200$) that are at least an order of magnitude greater than for pseudo O_h complexes ($\varepsilon = 10-20$)[24,26] so that transitions arising from the $(Tpm^*)_2Ni^{2+}$ complex in Zargarian's compound are likely completely obscured by the much more intense transitions derived from the $NiCl_4^{2-}$ ion also present in that solid in an equimolar amount. No intense features assignable to a NiX_4^{2-} chromophore are observed in the solid or solution phase spectra of $TpmNiX_2(H_2O)_n$. Rather, the electronic spectrum of our Tpm product is indicative of only six-coordinate nickel(II) as would be expected in the formula proposed here.

We tested the general utility of the method developed by Zargarian's group for the preparation of single ligand scorpionate-nickel complexes.[8] The preparation of Tpm*Ni-(κ^1-NO_3)(κ^2-NO_3) was successfully duplicated and confirmed by infrared spectroscopy. This method also works when a solution of Tpm* reacts with nickel(II) chloride (in place of nickel nitrate), resulting in the controlled formation of $Tpm^*NiCl_2(OH_2)_{1.5}$ as described in the Experimental Section above. However, reactions of Tpm and KTp* with nickel(II) nitrate in acetone failed to yield single-ligand products in either case; pale lavender two-ligand products precipitated for each ligand. Our method offers additional kinetic control afforded by the anionic tetrahalonickelate ion and lack of solvent interference from nitromethane. Results of reactions of KTp and KTp* with different nickel(II) salts are summarized in Supporting Information, Figures S5−S7. The kinetic stability of different single-ligand Tpm^RNi and Tp^RNi products is clearly demonstrated by their formation and isolation under controlled conditions.

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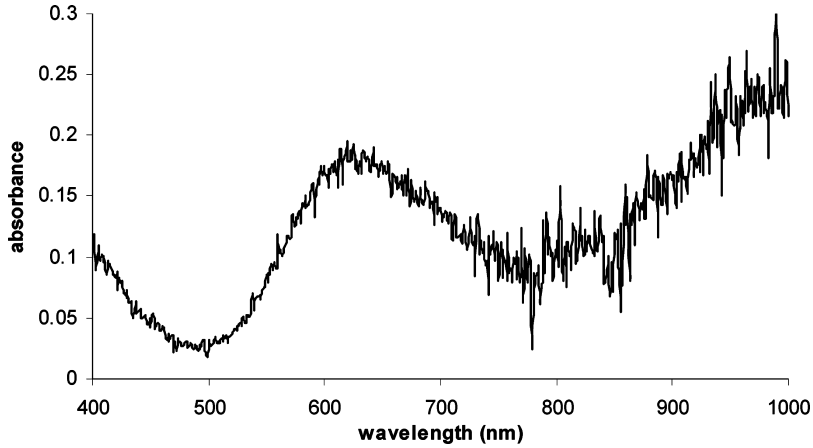

Figure 6. Diffuse reflectance electronic spectra of bead-TpmNiCl$_n$.

The utility of the scorpionate chelate makes this ligand class an excellent candidate for anchoring to synthesis beads or other solid supports. This ligand was anchored to polystyrene synthesis beads following the procedure outlined in Scheme 1. The presence of covalently linked Tpm on the beads, bead-Tpm, was determined by ^{13}C NMR (Supporting Information, Figure S3). To confirm that the Tpm was covalently linked to the beads and not merely embedded in the beads, a control experiment was performed in which Novasyn TG resin (terminated with -NH$_2$ functional group, which cannot react with the conjugate base of HOCH$_2$-Tpm), was used in a duplicate of the above synthesis. After workup, no peaks were found in the aromatic region of the ^{13}C spectrum, indicating that all unreacted material is removed from the beads by the washing procedure. Chemical evidence for covalently linked Tpm on the beads came when bead-Tpm was metallated. Treatment of bead-Tpm with a NiCl$_4^{2-}$/nitromethane solution resulted in an immediate color change for the beads from pale amber to green (Figure 5). These beads where thoroughly washed with nitromethane and ether, and their green color persisted throughout. As a control, the experiment was repeated using fresh Novasyn TG Bromo resin. No color change was observed (Figure 5), indicating that the binding that leads to the color change was caused by nickel interacting with Tpm and not with the poly(ethyleneglycol) tethers of the resin. Diffuse reflectance electronic spectra were recorded for these colored bead samples, with the unmetallated beads used as background. The green beads showed two broad bands that coincided with the two lowest energy spin allowed electronic transitions of a six coordinate nickel(II) center on the beads, very similar to those observed in solid TpmNiCl$_2$(OH$_2$)$_3$ (Figure 6).

Conclusions

We report here the first ever single-ligand Tpm complexes of nickel(II), TpmNiX$_2$(OH$_2$)$_n$ (X = Cl, Br). These single-ligand products were readily prepared by the direct reaction of the free ligand with NiX$_4^{2-}$ in nitromethane despite a complete lack of steric encumbrances on the ligand. This coordination mode was further extended to the first covalently immobilized Tpm-nickel(II) complexes. While this same method was also demonstrated to work with the more nucleophilic ligand, Tp*, it still failed to prevent the exclusive formation of two-ligand product, (Tp)$_2$Ni, when Tp was used.

The greater Lewis basicity of Tp* versus Tpm* or Tpm was evident in the different single-ligand coordination geometries that formed with nickel(II). Monoanionic Tp* produced the pseudotetrahedral nickel complex Tp*NiCl; however, both Tpm and Tpm* produced six coordinate pseudo-octahedral geometries, Tpm^{R}NiCl$_2$(OH$_2$). While the Tpm^{R}Ni^{2+} and Tp^{R}Ni$^+$ Lewis acid centers show varying kinetic stabilities once formed, the greater positive charge on nickel in the pyrazolylmethane cases causes Tpm^{R}Ni^{2+} to bind up to three additional ligands versus its less positively charged Tp^{R}Ni$^+$ counterpart. The different charges of these ligands have been shown to have a greater effect than the pyrazole ring substituents on the Lewis acidity of Tp^{R}M and Tpm^{R}M metal centers.[27]

Diminished solvent basicity and extensive halo-preligation of the nickel(II) center enable the direct reaction of scorpionate ligands (or ligand salts, KTp*) with this metal center to yield single-scorpionate products. This method is expected to become a useful route to single-scorpionate complexes for the majority of first row transition elements for which well defined MX$_4^{n-}$ ions are known.

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Supporting Information Available: Complete infrared spectra of all new compounds described in this work. Electronic spectra of Tp*NiCl$_2$(OH$_2$)$_{1.75}$ in the solid state and in aqueous solution. ^{13}C NMR spectrum bead-Tpm suspended in CDCl$_3$. Infrared spectra comparing the ν(B−H) bands for Tp*NiCl, (Tp*)$_2$Ni, and the mixture of the two formed from the room temperature reaction of KTp* with NiCl$_4^{2-}$ in nitromethane. Successive electronic spectra detailing the reactions of KTp and KTp* with Ni(NO$_3$)$_2$ and with NiCl$_2$ in THF. This material is available free of charge via the Internet at http://pubs.acs.org.

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