Sources of Naked Divalent First-Row Metal Ions: Synthesis and Characterization of $[M^{II}(NCMe)_6]^{2+}$ (M = V, Cr, Mn, Fe, Co, Ni) Salts of Tetrakis[3,5-bis(trifluoromethyl)phenyl]borate

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Abstract: $[M^{II}(NCMe)_6][TFPB]_2$ (M = V, Cr, Mn, Fe, Co, Ni; $[TFPB]^-$ = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate) were synthesized and characterized in the solid state and in solution. As a result of the extremely poor coordinating ability of $[TFPB]^-$, a wide redox-stable window, as well as chemically facile loss of the MeCN ligands, these salts are excellent sources of naked divalent first-row metal ions. Thermolysis up to 100 °C leads to the loss of one MeCN and formation of a η^2-bound nitrile, while addition of MeCN reforms $[M^{II}(NCMe)_6]^{2+}$. Above 130 °C decomposition occurs with loss of MeCN and abstraction of fluoride from the anion to form MF_2. The room temperature effective moments $[M^{II}(NCMe)_6][TFPB]_2$ are in the range typically found for other octahedral divalent salts of these metal ions, with values greater than the spin-only values observed for the Cr^{II}, Fe^{II}, Co^{II}, and Ni^{II} salts; these are ascribed to first- and second-order spin-orbit effects. The temperature dependence of the susceptibility for the Fe^{II} and the Co^{II} salts can be fit to expressions that include zero-field splitting (D) with $g = 2.4$, $D = -0.5$ K, and $\theta_{fit} = -5$ K for Fe^{II}, and $g = 2.0$, $D = -1$ K, $TIP = 50 \times 10^{-6}$ emu mol^{-1}, and $\theta_{fit} = -8$ K for Co^{II}. The infrared ν_2-CN absorption energies of the $[M^{II}(NCMe)_6][TFPB]_2$ salts qualitatively map with the predicted ligand field stabilization energy. In solution these salts exhibit electronic spectra consistent with octahedral cations. Ligand field splittings (Δ_o) range from 9600 (Co^{II}) to 14300 cm^{-1} (V^{II}) and are greater than those of the hexaaquo species and, where data is available, are slightly smaller than those of the hexaammine species. There is evidence in the electronic and infrared spectra for significant tetragonal distortion in the Cr^{II} salt.

Keywords: acetonitrile complexes · ligand field theory · magnetic properties · N ligands · transition metals

Introduction

Sources of metal ions that are soluble in nonaqueous solvents and possess very weakly or, ideally, noncoordinating, redox-stable anions are essential for developing many areas of chemistry, and we have found a particular need in the synthesis of many molecule-based magnetic materials.[1] The ability of a weak Lewis base to occupy a metal coordination site to create an extended lattice is often deterred by anions and/or solvent molecules that are more strongly coordinating. The synthesis of Prussian blue analogues, that is, 3-D network structures possessing $\cdots \rightarrow M \leftarrow C \equiv N \rightarrow M' \leftarrow N \equiv C \rightarrow M \leftarrow \cdots$ chains along all three bonding axes, in nonaqueous media is one situation in which anions such as $[CF_3SO_3]^-$ and $[BF_4]^-$, and solvents such as acetonitrile remain coordinated metal centers in Prussian blue type lattices, thus preventing complete formation of an extended lattice.[1] Since the nitrogen end of cyanide of a hexacyanometallate has a basicity comparable to that of ammonia in the spectrochemical series,[2] nucleophilic solvents of comparable basicity present in great excess can be difficult to fully displace by a hexacyanometallate in relatively dilute (stoichiometric) concentrations. Other nominally inert anions such as $[BPh_4]^-$ can reduce or chemically react with a metal center.[3]

Tetrakis[3,5-bis(trifluoromethyl)phenyl]borate ($[TFPB]^-$)[4] is an anion that avoids these limitations as it is essentially noncoordinating.[3a] Its salts are extremely soluble (even in diethyl ether) and it is redox stable between about 1.6 and −1.8 V vs Ag/AgCl(aq).[5] (In comparison, the $E_{1/2}$ for $[BPh_4]^-$ was reported to be about 0.5 V vs $Ag/AgNO_3$-(MeCN).[3b]) This anion can be prepared with many different cations, including K^+,[4] Ag^+,[5] Tl^+,[6] [tetraalkylammonium]$^+$,[7] and ferrocenium.[8] $[M^{II}(NCMe)_6][TFPB]_2$ (M = V, Cr, Mn, Fe, Co, Ni), as a result of their facile ability to lose MeCN, provide naked metal cation sources that are soluble in MeCN, THF, and even Et_2O and, along with their chemical and physical properties, are reported herein.

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Results and Discussion

Elemental analyses of $[M^{II}(NCMe)_6][TFPB]_2$ (M = V, Cr, Mn, Fe, Co, Ni) are consistent with the proposed formulation. These analyses are insensitive to the metal ion present since the molecular mass is very large, $>2000\,g\,mol^{-1}$, and varies only by the difference in the mass of the metal. Obtaining reasonable analyses was problematic owing to the ease of solvent loss at room temperature and combustion problems. Sample sizes of approximately <2 mg gave poor analyses, unusually high in %N, while larger samples gave more consistent results.[9] If one assumes less than six MeCN molecules in the molecular formula, the difference between the calculated and observed percent composition increases.

Thermal properties: Thermal gravimetric analyses (TGA) of $[M^{II}(NCMe)_6][TFPB]_2$ are qualitatively similar, but do show some differences (Figure 1; Table 1). Each salt has a small weight loss below 100 °C corresponding to the loss of ≤ 1 MeCN. Above 100 °C, however, between about 74 and 93 % weight loss occurs corresponding to both the loss of remaining MeCN and decomposition of the $[TFPB]^-$ anion. Closer inspection of this large weight loss region reveals one or two changes in slope that are consistent with different rates of desolvation and/or decomposition processes. Onset temperatures for these changes in rate of weight loss are summarized in Table 1, and range from 131 °C (Cr^{II}) to 146 °C (V^{II} and Ni^{II}).

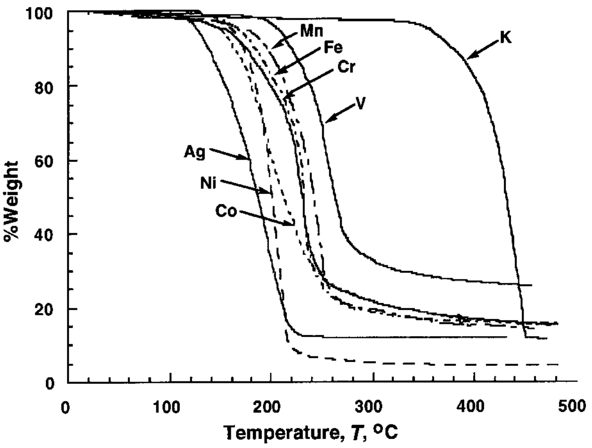


Figure 1. TGA of the K[TFPB], Ag[TFPB], and $[M^{II}(NCMe)_6][TFPB]_2$ salts.

Table 1. Thermal gravimetric analyses of the $[M^{II}(NCMe)_6][TFPB]_2$ salts up to 450 °C at 15 °C/ min.

	Weight loss < 100 °C		Weight loss > 100 °C			
	T_{onset} [°C]	% loss	T_{onset} [°C]	T_{onset} [°C]	T_{onset} [°C]	Total % loss
Ni	ambient	1.6	146	160	185	95.1
Co	ambient	1.4	145	[a]	168	85.5
Fe	ambient	1.5	143	180	221	84.4
Mn	[a]		139	167	220	84.2
Cr	ambient	2.2	131	159	211	85.1
V	ambient	0.8	146	160	231	74.3

[a] Not resolved.

The Ni^{II} salt decomposes the most completely leaving a light gray residue. The total weight loss observed (95.1 %) correlates well with that expected for residual NiF_2 (95.2 %). Hence, upon complete loss of solvent the active metal reacts with the nominally inert anion. The other salts retain more mass and leave black residues suggesting an incomplete and/or more complex decomposition reactions between the desolvated metal ion and the $[TFPB]^-$ anion. This is supported by the fact that when K[TFPB] is thermalized under the same conditions, there is no decomposition below about 340 °C (Figure 1). Ag[TFPB] also decomposes in the TGA leaving a white residue after an 87.8 % weight loss. This is in good agreement with the calculated weight loss of 86.9 % assuming AgF is the residue.

Fluoride abstraction from the CF_3 groups in $[TFPB]^-$ to form MF_2 (or MF) is facile in the solid state when the coordination sphere of the metal ion becomes vacant as a result of to solvent loss. Abstraction of fluoride from $[TFPB]^-$ has been observed to be quite efficient in the presence of trialkylsilanes in poorly coordinating solvents yielding fluorosilanes and triphenylmethane.[10] Aryl cations have recently been found to activate the F_2C-F bonds in $[TFPB]^-$ intermolecularly in solution.[11]

Infrared spectra: The infrared (IR) spectra of $[M^{II}(NCMe)_6][TFPB]_2$ as Nujol mulls exhibit two sharp ν_{CN} absorptions of medium, approximately equal intensity at 2320 and 2294 cm^{-1}, Table 2. The Cr^{II} salt is the only exception with an additional, weaker absorption at 2277 cm^{-1} also being present.

Table 2. Infrared ν_{CN} absorption bands of $[M^{II}(NCMe)_6][TFPB]_2$ compared to many of the known $[M^{II}(NCMe)_n](X)_2$ salts as Nujol mulls.

	Anion, X	ν_{CN} [cm^{-1}][a]			Ref.
Ni	[TFPB]	2326 (m)	2299 (m)		
	$[BF_4]$[b]	2316	2292		[12c]
Co	[TFPB]	2321 (m)	2295 (m)		
	$[BF_4]$[b]	2316	2292		[12c]
Fe	[TFPB]	2318 (m)	2291 (m)		
	$[BF_4]$[b]	2310	2287		[12c]
Mn	[TFPB]	2315 (m)	2289 (m)		
	$[BF_4]$[c]	2307	2282		[12c]
Cr	[TFPB]	2324 (m)	2297 (m)	2277 (w)	
	$[BF_4]$[c]	2333 (m)	2305 (m)		[15]
V	[TFPB]	2320 (m)	2291 (m)		
	$[BPh_4]$[b]	2310 (w)	2280 (m)		[28]

[a] Relative intensities are included as m (medium) and w (weak). [b] Six MeCNs coordinated to the metal ion. [c] Four MeCNs coordinated to the metal ion.

The absorptions for the $[TFPB]^-$ anion are typical for its salts.[4, 6–8] The two IR ν_{CN} absorption bands observed for free acetonitrile are assigned to the 2253 cm^{-1} fundamental ν_2-CN stretching mode and a combination mode ($\nu_3 + \nu_4$) at 2293 cm^{-1}.[12b, 13] These modes are similarly assigned to the coordinated acetonitrile. Free acetonitrile, however, is not present in the spectra. These assignments were made neglecting Fermi resonance effects.[12b, 13]

The presence of only two absorptions is consistent with high symmetry of the coordinated MeCNs about the metal center, that is, octahedral, tetrahedral, or square planar coordination.[14] Additional absorptions are expected for reduced-symmetry five- or three-coordinate MeCN adducts or octahedral complexes that have considerable Jahn–Teller (tetragonal) distortions. In the case of Cr^{II} the three-peak absorption pattern is reproducible in its relative intensities, suggestive of two weakly coordinating axial MeCNs (relative to the equatorial MeCNs) that are responsible for the weaker absorption at 2277 cm^{-1}. For D_{4h} $[Cr^{II}(NCMe)_4][BF_4]_2$ the $[BF_4]^-$ anions occupy the axial positions and the four equatorial MeCN ligands exhibit their ν_{CN} absorptions at 2333 and 2305 cm^{-1}.[15] Hence, the data is consistent with the $[Cr^{II}(NCMe)_6][TFPB]_2$ formulation. Additionally, there is evidence in the electronic spectrum for a considerable Jahn–Teller distortion for this ion, vide infra.

The energy of both IR ν_{CN} absorptions for the coordinated acetonitrile is higher than those of free acetonitrile. This is expected due to the σ donation of electron density from the nitrogen lone pair of the nitrile that has some antibonding character.[2, 16] Within the series of $[M^{II}(NCMe)_6][TFPB]_2$ (M = V, Cr, Mn, Fe, Co, Ni), the energy of both ν_{CN} absorptions decreases from Ni to Mn, then increases to Cr, and decreases again to V. The peak separation remains constant for all cases. This trend qualitatively maps with the ligand field stabilization energy with the exception of V^{II} (Figure 2) and is in accord with studies on the $[SbCl_6]^-$ and $[SnCl_6]^{2-}$ salts.[13b]

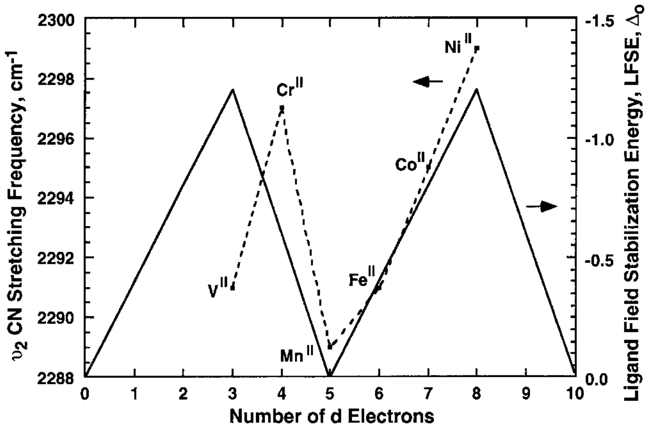
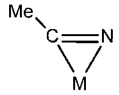


Figure 2. ν_2-CN stretching frequency (labeled points) and predicted ligand field stabilization energy (LFSE, solid line) as a function of the number of d electrons for $[M^{II}(NCMe)_6][TFPB]_2$.

When these salts are allowed to stand at room temperature for extended periods of time (hours), solvent is lost and an additional IR absorption grows in at 1731 cm^{-1}. This change occurs most rapidly in the V^{II} salt, but is observed for all salts. When a sample has undergone this change, it can be recrystallized to reform the original hexacoordinate compound. The source of this absorption is unknown, but based on its energy it is assigned to a η^2-bound nitrile, **1**. This assignment is consistent with the known η^2-bound nitrile ν_{CN} absorptions ranging from 1725 to 1766 cm^{-1}.[17] The $[M^{II}(NCMe)_6]^{2+}$ salts with more strongly coordinating anions, for example, $[CF_3SO_3]^-$ and $[BF_4]^-$, do not show evidence for this behavior as these anions will occupy the vacant coordination sites.



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Electronic structure: Acetonitrile solutions of $[M^{II}(NCMe)_6][TFPB]_2$ exhibit electronic absorption spectra that are consistent with divalent metal ions in an octahedral ligand field environment.[12, 18, 19] The electronic absorptions are comparable with those of the $[M^{II}(OH_2)_6]^{2+}$ ions, but are shifted to higher energies by 900 to 4000 cm^{-1} (Table 3).

Table 3. Summary of electronic spectra for $[M^{II}(NCMe)_6][TFPB]_2$ in MeCN

	Observed values for $[M^{II}(NCMe)_6]^{2+}$			Reported values and assignments for $[M^{II}(OH_2)_6]^{2+}$ [12, 19, 23]			
	λ_{max} [cm^{-1}]	ε [$M^{-1}cm^{-1}$][a]	Δ_o [cm^{-1}]	λ_{max} [cm^{-1}]	ε [$M^{-1}cm^{-1}$]	Δ_o [cm^{-1}]	Assignment
Ni[c]	10400	7.1	10400	8700	1.6	8700	$^3T_{2g}(F) \leftarrow {}^3A_{2g}(F)$
	17200	5.8		14500	2.0		$^3T_{1g}(F) \leftarrow {}^3A_{2g}(F)$
	27500	8.0		25300	4.6		$^3T_{1g}(P) \leftarrow {}^3A_{2g}(F)$
Co[d]	9200	5.2	9600	8000	1.3	9300	$^4T_{2g}(F) \leftarrow {}^4T_{1g}(F)$
	20300	14.3		19600	4.8		$^4A_{2g}(F) \leftarrow {}^4T_{1g}(F)$
	21200	14.7		21600	2.1		$^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$
Fe	10900	9.2	10900	10000	1.1	10000	$^5E_g \leftarrow {}^5T_{2g}$
Mn	15100	≈0.2	11100	18600	0.013	8500	$^4T_{1g}(G) \leftarrow {}^6A_{1g}$
	19100	≈0.3		22900	0.009		$^4T_{2g}(G) \leftarrow {}^6A_{1g}$
	unresolved			24900	0.031		$^4E_g(G) \leftarrow {}^6A_{1g}$
	unresolved			25150	0.014		$^4A_{1g}(G) \leftarrow {}^6A_{1g}$
	23700	≈0.5		27900	0.018		$^4T_{2g}(D) \leftarrow {}^6A_{1g}$
	26900	≈0.6		29700	0.013		$^4E_g(D) \leftarrow {}^6A_{1g}$
	unresolved			32400	0.02		$^4T_{1g}(P) \leftarrow {}^6A_{1g}$
Cr	9000	1.8	15500	9500	2.0	14000	[b]
	15500	12.7		14000	5.2		$^5T_{2g} \leftarrow {}^5E_g$
V	16300	46.3	16300	12300	4.1	12300	$^4T_{2g}(F) \leftarrow {}^4A_{2g}(F)$
	22500	46.3		18500	6		$^4T_{1g}(F) \leftarrow {}^4A_{2g}(F)$

[a] Concentrations were 1–2.5 mM in MeCN; path length of 5 cm; background was solvent vs solvent; $[TFPB]^-$ cutoff above 33000 cm^{-1}. [b] Forbidden transition due to tetragonal distortion of the octahedral coordination sphere.[12e] [c] The corresponding absorptions (and ε) for $[Ni^{II}(NH_3)_6]^{2+}$ are 10800 cm^{-1} (4.0 $M^{-1}cm^{-1}$), 17500 cm^{-1} (4.8 $M^{-1}cm^{-1}$), and 28200 cm^{-1} (6.3 $M^{-1}cm^{-1}$) reflecting a Δ_o of 10800 cm^{-1}.[21] [d] The corresponding absorptions (and ε) for $[Co^{II}(NH_3)_6]^{2+}$ are 9000 cm^{-1} (3 $M^{-1}cm^{-1}$), 18500 cm^{-1} (4 $M^{-1}cm^{-1}$), and 21100 cm^{-1} (8 $M^{-1}cm^{-1}$) reflecting a Δ_o of 10200 cm^{-1}.[21]

Hence, the transition assignments for the absorptions are the same for both the hexaaquo and the hexakis(acetonitrile) ions. The electronic spectra of the $[M^{II}(NCMe)_6]^{2+}$ ions are shown in Figure 3, and the ligand field splitting values (Δ_o, Table 3) are calculated by means of the absorption λ_{max} energies and graphical interpolation of the Tanabe–Sugano diagrams.[20] The Δ_o's range from 9600 (Co^{II}) to 14300 cm^{-1} (V^{II}) as $V^{II} > Cr^{II} > Mn^{II} > Fe^{II} > Ni^{II} > Co^{II}$. This differs from the $Cr^{II} > V^{II} > Fe^{II} > Co^{II} > Ni^{II} > Mn^{II}$ ordering observed for $[M^{II}(OH_2)_6]^{2+}$.[12a] The molar extinction coefficients (ε) range from 0.2 to 46 $cm^{-1}M^{-1}$.

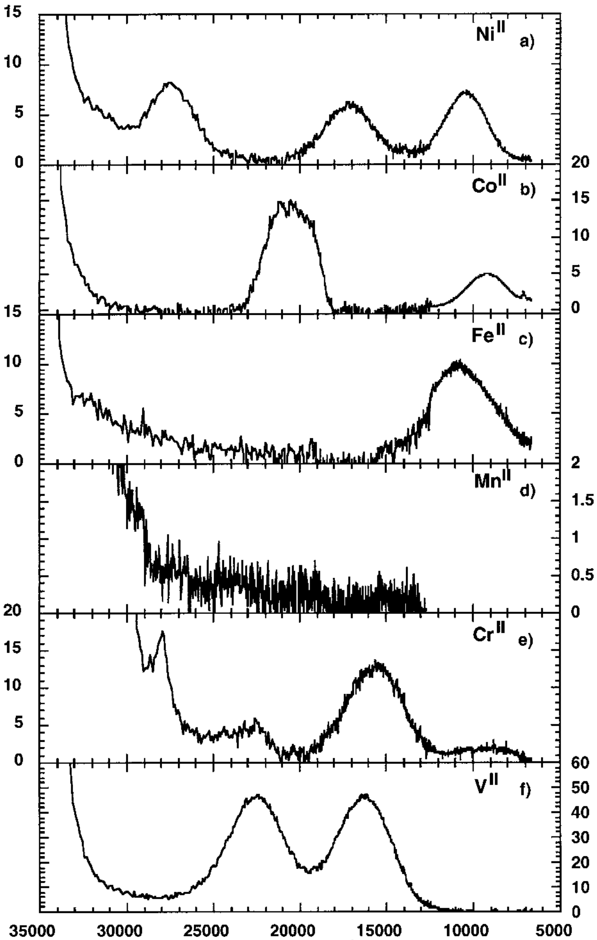

Figure 3. Electronic absorption spectra of the $[M^{II}(NCMe)_6][TFPB]_2$ salts in MeCN ($b = 5$ cm). a) Ni^{II}, 2.435 mM, b) Co^{II}, 1.240 mM; c) Fe^{II}, 1.244 mM; d) Mn^{II}, 2.261 mM (three scans averaged between 12500 and 35000 cm^{-1}); e) Cr^{II}, 0.982 mM (absorptions at 22600 and 28000 cm^{-1} are due to about 4% Cr^{III} from air oxidation); f) V^{II}, 0.990 mM.

In general, the electronic spectra are very comparable to the $[M^{II}(OH_2)_6]^{2+}$[19, 21] and other weak field per-ligated octahedral cationic complexes with ligands such as ammonia,[21] nitromethane,[12d] ethylacetate,[12d] and pyridine.[22] The values of Δ_o for the $[M^{II}(NCMe)_6]^{2+}$ ions in most cases are considerably larger than those of the $[M^{II}(OH_2)_6]^{2+}$ ions; this is in agreement with acetonitrile being a stronger field ligand than water in the spectrochemical series. In the context of a Prussian blue lattice, the weak field ligand site $[M(NC)_6]^{n+}$ has been reported to have a ligand field strength comparable to that of ammonia.[2] The reported Δ_o values for $[Ni^{II}(NH_3)_6]^{2+}$ and $[Co^{II}(NH_3)_6]^{2+}$ (10800 and 10200 cm^{-1}, respectively[21a]) are slightly greater than the Δ_o values found for the hexakis(acetonitrile) adducts (10400 and 9600 cm^{-1}, respectively). Hence, MeCN falls between H_2O and NH_3 in the spectrochemical series.[12a] Consequently, the ability of these ions to dissolve in solvents other than acetonitrile, which can compete with a hexacyanometallate for coordination to a metal ion, is important to enhance the formation of an extended Prussian blue lattice.

The molar extinction coefficients (ε) of the Laporte (symmetry) forbidden d→d transitions for the $[M^{II}(NCMe)_6]^{2+}$ ions are greater than those of the $[M^{II}(OH_2)_6]^{2+}$ ions. This is ascribed to an increase in vibronic coupling of coordinated MeCN with respect to water;[2,19] this also contributes to the larger Δ_o values. The stronger vibrational coupling, together the greater polarizability of acetonitrile with respect to water, leads to a larger vibrational modulation of the crystal field and a greater breakdown of the Laporte selection rule for transitions that are ligand field dependent, thus leading to greater ε values.[19] This effect is also seen for the very weakly absorbing Mn^{II} ion with transitions that are both Laporte and spin forbidden.

The electronic spectrum of $[Cr^{II}(NCMe)_6]^{2+}$, like $[Cr^{II}(OH_2)_6]^{2+}$, exhibits a weak absorption at 9000 cm^{-1} ($\varepsilon = 1.8\ cm^{-1}M^{-1}$) attributed to a low energy transition in a tetragonally distorted cubic d-orbital manifold (Figure 3e).[12e] The tetragonal distortion is consistent with the observation of a third, minor IR ν_{CN} absorption, vide supra, with the two axial MeCN ligands being less strongly bound than the equatorial ligands. At higher energy there are absorptions that are due to about 4% Cr^{III} contaminant as a result of oxidation. The amount of contaminant varies from spectrum to spectrum suggesting that oxidation occurs during acquisition of the spectra and that impurities are not inherent to the compound. Upon air exposure, solutions quickly turn green and the resulting spectra are of the contaminant Cr^{III} species (Figure 4).

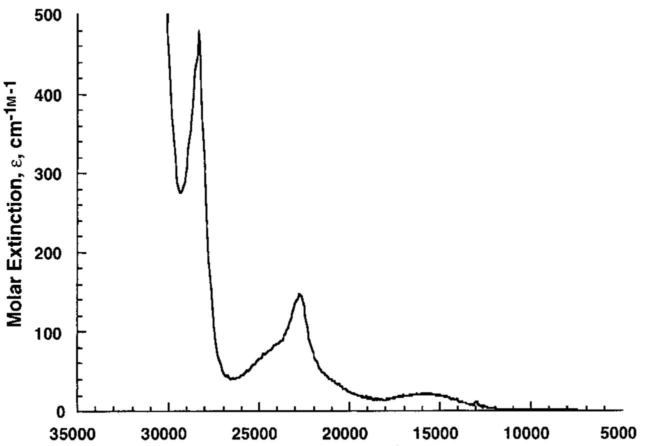

Figure 4. Electronic absorption spectrum of $[Cr^{II}(NCMe)_6][TFPB]_2$ in MeCN oxidized in air for about 10 min.

Magnetic properties: The room temperature effective magnetic moments (μ_{eff}, $\equiv[8\chi T]^{1/2}$) of $[\text{M}^{\text{II}}(\text{NCMe})_6][\text{TFPB}]_2$ are presented in Table 4. μ_{eff} are calculated from the measured molar susceptibility (χ) based on the above proposed formula assuming a Landé g value of 2.[23] Only for the V^{II} and Mn^{II} salts are the values of μ_{eff} consistent with the expected spin only values.[12a,b, 18] The other salts have μ_{eff}'s exceeding the spin only values, but are within the range of what is commonly observed for these ions, Table 4.[12] For M = Ni the observed moment is 3.31 μ_{B} vs the calculated spin-only value of 2.83 μ_{B}. However, it is comparable with 3.20,[12a] 3.23,[12b] and 3.22 μ_{B},[12c] reported for $[\text{Ni}^{\text{II}}(\text{NH}_3)_6]^{2+}$, $[\text{Ni}^{\text{II}}(\text{NCMe})_6]\text{Br}_2$, and $[\text{Ni}^{\text{II}}(\text{NCMe})_6][\text{BF}_4]_2$, respectively. Likewise, the moments for M = Co, Fe, and Cr are 5.31, 5.85, and 5.09 μ_{B}, respectively, in good agreement with those of $[\text{Co}^{\text{II}}(\text{NCMe})_6][\text{BF}_4]_2$ (5.18 μ_{B}[12c]), $[\text{Fe}^{\text{II}}(\text{NCMe})_6][\text{BF}_4]_2$ (5.42[12c] and 5.59 μ_{B}[12d]), and $[\text{Cr}^{\text{II}}(\text{OH}_2)_6]\text{Br}_2$ (4.90 μ_{B}[12e]). These values exceed the spin-only values because the T ground states for high-spin octahedral Co^{II} and Fe^{II} are subject to large first-order spin-orbit coupling effects, while the T excited states of Ni^{II} and Cr^{II} contribute second-order spin-orbit coupling to give substantial zero-field splitting and is reflected in g values greater than 2. Modeling of the spin-orbit coupling parameters for the cubic-field $^4\text{T}_{1g}$ and $^5\text{T}_{2g}$ terms[24] may account for the magnetic behavior of these ions.

Table 4. Room temperature effective moments (μ_{B}) of $[\text{M}^{\text{II}}(\text{NCMe})_6][\text{TFPB}]_2$.

	μ_{eff} (observed)[a]	μ_{eff} [12, 18, 28] (typical values)	μ_{eff} (spin only)	G.S. →E.S.[b]
Ni[c]	3.31 (1)	2.8–3.5	2.83	$^3\text{A}_2\rightarrow{}^3\text{T}_2$
Co[d]	5.38 (1)	4.7–5.5	3.87	$^4\text{T}_1\rightarrow{}^4\text{T}_2$
Fe[e]	5.85 (1)	5.0–5.9	4.90	$^5\text{T}_2\rightarrow{}^5\text{E}$
Mn[f]	5.98 (2)	5.6–6.1	5.92	$^6\text{A}_1$
Cr[g]	5.09 (3)	4.8–5.0	4.90	$^5\text{E}\rightarrow{}^5\text{T}_2$
V[h]	3.92 (1)	3.8–4.0	3.87	$^4\text{A}_2\rightarrow{}^4\text{T}_2$

[a] Each entry is an average of four measurements at 300 K. Numbers in parentheses are estimated standard deviations of the measurements in the least significant digits. [b] First spin-allowed electronic transition. [c] The μ_{eff} reported for $[\text{Ni}^{\text{II}}(\text{NH}_3)_6]^{2+}$, $[\text{Ni}^{\text{II}}(\text{NCMe})_6]\text{Br}_2$, and $[\text{Ni}^{\text{II}}(\text{NCMe})_6][\text{BF}_4]_2$ are 3.20,[12a] 3.23,[12b] and 3.22 μ_{B},[12c] respectively. [d] The μ_{eff} reported for $[\text{Co}^{\text{II}}(\text{NCMe})_6][\text{BF}_4]_2$ is 5.18 μ_{B}.[12c] [e] The μ_{eff} reported for $[\text{Fe}^{\text{II}}(\text{NCMe})_6][\text{BF}_4]_2$ are 5.42 [12c] and 5.59 μ_{B}.[12d] [f] The μ_{eff} reported for $[\text{Mn}^{\text{II}}(\text{NCMe})_4][\text{BF}_4]_2$ is 5.90 μ_{B}.[12c] [g] The μ_{eff} reported for $[\text{Cr}^{\text{II}}(\text{OH}_2)_6]\text{Br}_2$ is 4.90 μ_{B}.[12e] [h] The μ_{eff} reported for $[\text{V}^{\text{II}}(\text{NCMe})_6][\text{BPh}_4]_2$ and $[\text{NH}_4]_2[\text{V}^{\text{II}}(\text{OH}_2)_6][\text{SO}_4]_2$ are 4.0 [28] and 3.76 μ_{B},[18] respectively.

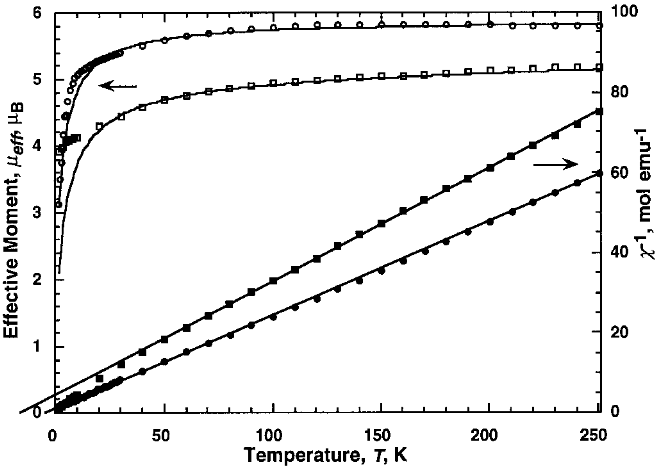

Figure 5. Temperature dependent μ_{eff} (○, □) and $1/\chi$ curves (○, ■) for $[\text{Fe}^{\text{II}}(\text{NCMe})_6][\text{TFPB}]_2$ (○, ●) and $[\text{Co}^{\text{II}}(\text{NCMe})_6][\text{CF}_3\text{SO}_3]_2$ (□, ■). The solid lines are fits to Equations (1) and (2) (see text).

$\chi(T)$ of $[\text{Co}^{\text{II}}(\text{NCMe})_6][\text{CF}_3\text{SO}_3]_2$[25] and $[\text{Fe}^{\text{II}}(\text{NCMe})_6][\text{TFPB}]_2$ were measured between 2 and 250 K and are plotted as $\chi^{-1}(T)$ and $\mu_{\text{eff}}(T)$ (Figure 5).[26] $\chi^{-1}(T)$ is linear and was fit to the Curie–Weiss expression $[\chi\propto g^2(T-\theta)^{-1}]$ with $g=2$ and $\theta=-4$ K for Co^{II}, and $g=2.4$ and $\theta=-12$ K for Fe^{II}, suggesting weak antiferromagnetic coupling. The $\mu_{\text{eff}}(T)$ of the Co^{II} and Fe^{II} salts decrease with decreasing temperature from 5.20 and 5.85 μ_{B} to 3.91 and 3.12 μ_{B}, respectively, at 2 K suggestive of zero-field splitting.[27] Above 20 K the Fe^{II} and Co^{II} could be fit to Equations (1) and (2),[27] respectively, with

$$\chi=3N_{g}^{2}\ \frac{\mu_{\text{B}}^{2}}{4kT}\left(\frac{1+9\,\text{e}^{-2\frac{D}{kT}}}{1+\text{e}^{-2\frac{D}{kT}}}+\frac{8+6\frac{kT}{D}\left(1-\text{e}^{-2\frac{D}{kT}}\right)}{1+2\,\text{e}^{-2\frac{D}{kT}}}\right)+\text{TIP} \tag{1}$$

$$\chi=\left(2N_{g}^{2}\ \frac{\mu_{\text{B}}^{2}}{3kT}\right)\frac{\left(\text{e}^{-\frac{D}{kT}}+4\,\text{e}^{-4\frac{D}{kT}}\right)+\left(6\frac{kT}{D}\left(1+\text{e}^{-\frac{D}{kT}}\right)+4\frac{kT}{3D}\left(\text{e}^{-\frac{D}{kT}}-\text{e}^{-4\frac{D}{kT}}\right)\right)}{1+2\,\text{e}^{-\frac{D}{kT}}+2\,\text{e}^{-4\frac{D}{kT}}}+\text{TIP} \tag{2}$$

$g=2.4$, D (zero-field splitting parameter) $=-0.5$ K, $\theta_{\text{fit}}=-5$ K, and no temperature independent paramagnetism (TIP) for Fe^{II}, and $g=2.0$, $D=-1$ K, $\text{TIP}=50\times10^{-6}$ emu mol^{-1}, and $\theta_{\text{fit}}=-8$ K for Co^{II} (Figure 5). The θ-values obtained from the Curie–Weiss fits are in reasonable agreement with those obtained from Equations (1) and (2), as are the g values. Below 20 K the data for both Fe^{II} and Co^{II} deviate from calculations and have a change in slope in the $\text{d}\mu(T)/\text{d}T$ data, suggesting a phase transition or onset of differing phenomena.

Conclusion

$[\text{M}^{\text{II}}(\text{NCMe})_6][\text{TFPB}]_2$ (M = V, Cr, Mn, Fe, Co, and Ni) have been prepared and characterized. This formulation is similar to that found in the hexakis(acetonitrile) Ni^{II} and Co^{II} salts when $[\text{CF}_3\text{SO}_3]^-$ and $[\text{BF}_4]^-$ are the anions;[12, 15] however, the Mn^{II}, and Cr^{II} salts have the formula $[\text{M}^{\text{II}}(\text{NCMe})_4][\text{X}]_2$ when X is $[\text{BF}_4]^-$.[12c, 15] For these $[\text{BF}_4]^-$ salts the more strongly coordinating anions occupy the axial coordination positions. Solution spectra show that these are all high spin, octahedral, divalent metal solvates except for Cr^{II}, which has a resolvable Jahn–Teller (tetragonal) distortion. Estimated values of Δ_{o} for these complexes, which range from 9600 cm^{-1} (Co^{II}) to 16300 cm^{-1} (V^{II}), show that acetonitrile has a greater ligand field strength than water in the hexaaquo complexes and falls slightly under NH_3 in the spectrochemical series.[19]

Upon loss of approximately one MeCN ligand, a terminal NCMe ligand chelates and becomes an η^2 nitrile that becomes terminal again upon addition of MeCN. Upon thermal treatment, fluoride abstraction from the $[\text{TFPB}]^-$ anion occurs together with solvent loss from the coordination sphere. When stored cold, because of the lability of the

MeCN ligands, these salts are useful sources of naked divalent transition metal cations with good solubility and noninteracting anions in nonaqueous media.

Experimental Section

General: All manipulations were performed under nitrogen or argon with standard Schlenk techniques in a Vacuum Atmospheres inert atmosphere DriLab. Dichloromethane was dried and distilled under nitrogen from CaH_2. Acetonitrile was dried and twice distilled under N_2 from CaH_2. Diethyl ether and tetrahydrofuran were dried and distilled under nitrogen from sodium benzophenone ketyl radical.

Materials: The $[V(NCMe)_6][BPh_4]_2$,[28] $[Cr(NCMe)_4][BF_4]_2$,[15] and potassium tetrakis[3,5-bis(trifluoromethyl)]phenyl]borate[29] were synthesized as previously described. $Ag[CF_3SO_3]$, $[(Ph_3P)_2N]Cl$, $[n\mathrm{Bu}_4N]Cl$, $[Et_4N]Cl$ (Aldrich), $AgNO_3$ (Alfa), $MnCl_2$ (Allied Chemical), $NiCl_2$, $CoCl_2$, and $FeBr_2$ (Mallinckrodt) were used as received. Owing to solvent loss, $[M^{II}(NCMe)_6][TFPB]_2$ (M = V, Cr, Mn, Fe, Co, Ni) must be stored cold.

Spectroscopic measurements: IR spectra were recorded on a BioRad Model FTS-40 spectrophotometer with $\pm 1\ cm^{-1}$ resolution. Samples were analyzed as Nujol and Fluorolube mulls between NaCl plates. UV/Vis/NIR spectra [250 to 1900 nm (5250–40 000 cm^{-1})] were recorded on a Cary-17D spectrophotometer with an On-Line Instrument Systems interface. Solution spectra were measured in quartz cells with a 5 cm path length. The solvent, MeCN, was purified as described above.

Thermal measurements: Elemental analyses were performed on freshly prepared samples hermetically sealed under argon in tin capsules and combusted in a Perkin Elmer, model 2400, elemental analyzer. Thermal properties of materials were studied on a TA Instruments Model 2910 differential scanning calorimeter (DSC) and a TA Model 2050 thermal gravimetric analyzer (TGA). The DSC was equipped with a LNCA liquid N_2 cooling accessory enabling operation between −150 and 500 °C with a modulated cell or up to 725 °C with a standard DSC cell. The TGA operates between ambient and 1000 °C and was located in a Vacuum Atmospheres inert atmosphere DriLab to study oxygen and moisture sensitive samples. DSC samples were weighed and hermetically sealed in aluminum pans in an argon atmosphere. TGA samples were handled in an argon atmosphere and heated under a nitrogen purge. Sample sizes were between 0.8 and 2 mg. Heating rates were $15\,^{\circ}C\,min^{-1}$ for TGA and $5\,^{\circ}C\,min^{-1}$ for DSC experiments.

Magnetic measurements: Magnetic susceptibility measurements were made between 2 and 300 K using a Quantum Design MPMS-5 5T SQUID magnetometer with a sensitivity of 10^{-8} emu (or 10^{-12} emu Oe^{-1} at 1 T) and equipped with the ultra-low field (≈ 0.005 Oe) accessory, reciprocating sample measurement system, and continuous low temperature control with enhanced thermometry features. Core diamagnetic contributions were calculated from standard tables and range from -976×10^{-6} emu mol^{-1} (Ni^{II} salt) to -979×10^{-6} emu mol^{-1} (V^{II} salt).

$Ag[B\{C_6H_3(CF_3)_2\}_4]$: A dry MeCN (7 mL) solution of $Ag(NO_3)$ (1.086 mmol, 0.1846 g) was added to a MeCN (10 mL) solution of $K[B\{C_6H_3(CF_3)_2\}_4]$[29] (1.109 mmol, 1.000 g). A white precipitate of KNO_3 began to form immediately. This was stirred for ≈10 min and Et_2O was added to help precipitate KNO_3, which was removed by filtration. The filtrate was concentrated in vacuo to dryness (without heating above ca. 80 °C). The solid was redissolved in CH_2Cl_2 while minimizing light exposure, and the remaining KNO_3 removed by filtration. The filtrate was layered with hexanes and kept at −30 °C to recrystallize the product. 0.834 g of colorless prisms were isolated (79 % yield) that clouded slightly when dried. IR(Nujol): $\tilde{\nu} = 1609$ (m), 1357 (s), 1281 (vs), 1144 cm^{-1} (vs); TGA: 87.8 % weight loss between 122 °C (T_{onset}) and 250 °C leaving a white residue; calcd 86.9 % weight loss for AgF as residue $Ag[B\{C_6H_3(CF_3)_2\}_4]$; $AgBC_{33.68}H_{14.24}F_{24}$ (993.51): calcd C 40.65, H 1.61; found C 40.55, H 1.84.

$[Ni^{II}(NCMe)_6][B\{C_6H_3(CF_3)_2\}_4]_2$: A dry MeCN (15 mL) solution of $Ag[B\{C_6H_3(CF_3)_2\}_4]$ (1.332 mmol, 1.294 g) was added to $NiBr_2$ (0.6662 mmol, 0.4156 g) and the mixture was stirred at room temperature in darkness for 12 h. The AgBr was filtered off leaving a sky-blue filtrate. This was concentrated in vacuo to 6 mL and cooled to −35 °C, and 1.100 g of pale blue-purple needles were formed (81 % yield). The product was stored at −40 °C. IR (Nujol): $\tilde{\nu}_{CN} = 2326$ (m), 2299 cm^{-1} (m); TGA: 95.1 % weight loss between room temperature and 450 °C leaving a light gray residue; calcd 95.2 % weight loss for NiF_2 as residue; $B_2C_{76}F_{48}H_{42}N_6Ni$ (2031.42): calcd C 44.92, H 2.08, N 4.14; found C 44.87, H 2.14, N 4.89.

$[Co^{II}(NCMe)_6][B\{C_6H_3(CF_3)_2\}_4]_2$: A dry MeCN (15 mL) solution of $Ag[B\{C_6H_3(CF_3)_2\}_4]$ (1.280 mmol, 1.243 g) was added to $CoCl_2$ (0.640 mmol, 0.0831 g) and the mixture stirred at room temperature in darkness for 12 h. The AgCl was filtered off leaving a pink filtrate. This was concentrated in vacuo to 6 mL and cooled to −35 °C, and 1.057 g of pale pink needles were formed (81 % yield). The product was stored at −40 °C. IR (Nujol): $\tilde{\nu}_{CN} = 2321$ (m), 2295 cm^{-1} (m); TGA: 85.5 % weight loss between room temperature and 450 °C leaving a black residue; $B_2C_{76}CoF_{48}H_{42}N_6$ (2031.66): calcd C 44.92, H 2.08, N 4.14; found C 44.09, H 2.04, N 4.17.

$[Fe^{II}(NCMe)_4][B\{C_6H_3(CF_3)_2\}_4]_2$: A dry MeCN (15 mL) solution of $Ag[B\{C_6H_3(CF_3)_2\}_4]$ (1.357 mmol, 1.317 g) was added to $FeBr_2$ (0.6784 mmol, 0.1463 g) and the mixture was stirred at room temperature in darkness for 12 h. The AgBr was filtered off leaving a pale yellow filtrate. This was concentrated in vacuo to 6 mL and cooled to −35 °C, and 1.090 g of colorless needles were formed (83 % yield). The product was stored at −40 °C. IR (Nujol): $\tilde{\nu}_{CN} = 2318$ (m), 2291 cm^{-1} (m); TGA: 84.4 % weight loss between room temperature and 450 °C leaving a black residue; $B_2C_{76}F_{48}FeH_{42}N_6$ (2028.58): calcd C 45.00, H 2.09, N 4.14; found C 43.86, H 1.88, N 4.29.

$[Mn^{II}(NCMe)_6][B\{C_6H_3(CF_3)_2\}_4]_2$: A dry MeCN (15 mL) solution of $Ag[B\{C_6H_3(CF_3)_2\}_4]$ (1.283 mmol, 1.245 g) was added to $MnCl_2$ (0.641 mmol, 0.0807 g) and the mixture was stirred at room temperature in darkness for 12 h. The AgCl was filtered off leaving a pale pink filtrate. This was concentrated in vacuo to 6 mL and cooled to −35 °C, and 0.983 g of colorless fine needles were formed (76 % yield). The product was stored at −40 °C. IR (Nujol): $\tilde{\nu}_{CN} = 2315$ (m), 2289 cm^{-1} (m); TGA: 84.2 % weight loss between room temperature and 450 °C leaving a black residue; $B_2C_{76}F_{48}H_{42}MnN_6$ (2027.67): calcd C 45.02, H 2.09, N 4.14; found C 45.29, H 2.00, N 4.57.

$[Cr^{II}(NCMe)_6][B\{C_6H_3(CF_3)_2\}_4]_2$: A dry THF (5 mL) solution of $K[B\{C_6H_3(CF_3)_2\}_4]$ (0.9880 mmol, 0.8913 g) was added to a THF/MeCN (6 mL, 5:1) solution/suspension of $[Cr(NCMe)_4][BF_4]_2$ (0.4940 mmol, 0.1926 g). The remaining $[Cr(NCMe)_4][BF_4]_2$ solid dissolved upon addition and a white precipitate of $K[BF_4]$ formed. The reaction mixture was stirred for 4 h at room temperature and then filtered. The filtrate was concentrated in vacuo to dryness, and the sky-blue solid redissolved in MeCN to crystallize the product at −35 °C. 0.742 g of sky-blue fine needles were recovered (74 % yield). The product was stored at −40 °C. IR (Nujol): $\tilde{\nu}_{CN} = 2324$ (m), 2297 (m), 2277 cm^{-1} (w); TGA: 85.1 % weight loss between room temperature and 450 °C leaving a black residue; $B_2C_{76}CrF_{48}H_{42}N_6$ (2024.73): C 45.08, H 2.09, N 4.15; found C 45.40, H 2.28, N 5.59.

$[V^{II}(NCMe)_6][B\{C_6H_3(CF_3)_2\}_4]_2$: A dry $MeCN/CH_2Cl_2$ (20 mL, 1:1) solution of $[(Ph_3P)_2N][B\{C_6H_3(CF_3)_2\}_4]$ (1.315 mmol, 1.843 g) was added to a stirred MeCN (40 mL) solution/suspension of $[V(NCMe)_6][BPh_4]_2$ (0.6413 mmol, 0.6001 g). The remaining solid $[V(NCMe)_6][BPh_4]_2$ dissolved rapidly on addition of the anion solution and $[(Ph_3P)_2N][BPh_4]$ crystallized out of solution. After 20 min the solution was concentrated in vacuo to 15 mL and filtered to remove $[(Ph_3P)_2N][BPh_4]$. The blue solution was cooled to −35 °C, and 0.888 g of aqua-blue needles were formed (68 % yield). The product was stored at −40 °C. IR (Nujol): $\tilde{\nu}_{CN} = 2320$ (m), 2291 cm^{-1} (m); TGA: 74.3 % weight loss between room temperature and 450 °C leaving a black residue; $B_2C_{76}F_{48}H_{42}N_6V$ (2023.68): calcd C 45.11, H 2.09, N 4.15; found C 44.49, H 2.06, N 4.25.

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