Chapter Two

USEFUL REAGENTS AND LIGANDS

11. HOMOLEPTIC TRANSITION METAL ACETONITRILE CATIONS WITH TETRAFLUOROBORATE OR TRIFLUOROMETHANESULFONATE ANIONS

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Transition metal cations solvated by weakly coordinating solvents are useful precursors for a variety of nonaqueous synthetic applications. The dissociation of acetonitrile ligands opens up vacant coordination sites for catalysis,1,2 and allows transition metals to be introduced into extended arrays formed by condensation reactions with polydentate ligands.3−5 Although salts of homoleptic acetonitrile metal cations with tetrafluoroborate anions have been known since the 1960s, there has been no detailed description of the syntheses and characterization of these compounds.6 Likewise, there have been general descriptions of the syntheses of trifluoromethanesulfonate salts, but no specific outline for individual metals has been published.7 In this report, the syntheses of [MII(CH3CN)5][BF4]2 (M = Cr,Mn,Fe,Co,Ni,Cu) and [MII(CH3CN)6][SO3CF3]2 (M = Mn,Fe,Co,Ni) are described. Two different methods are used to prepare tetrafluoroborate salts: (1) the oxidation of metals with nitrosonium tetrafluoroborate, first described by Hathaway et al.,8 and (2) the dehydration of aqueous tetrafluoroborate salts in a Soxhlet extractor with molecular sieves. The oxidation reaction is rapid, anhydrous, and recommended for smaller-scale preparations because of the relatively

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high cost of NOBF₄. The water dehydration method is slow, but is recommended for larger reaction scales and for those concerned with cost. Alternative water dehydration methods using triethylorthoformate or acetic anhydride were reported by Driessen and Reedijk.⁹ The trifluoromethanesulfonate derivatives are prepared by dissolution of the anhydrous salts M(SO₃CF₃)₂ in CH₃CN.

Materials and General Procedures

Acetonitrile was dried by distillation over 3-Å molecular sieves that had been activated by heating in a column to 200°C under a stream of dry nitrogen gas. All other solvents used in the syntheses were dried with appropriate drying agents and freshly distilled before use. Manganese chips (99%), iron chips (99%), cobalt (99.5%), nickel powder (99.99%), and copper (99%) were purchased from Aldrich Chemical Company. The reagents nitrosonium tetrafluoroborate, NOBF₄, and tetrafluoroboric acid, HBF₄ (48–50%), were obtained from commercial sources. [M(H₂O)ₓ]BF₄ salts of Fe(II), Co(II), Ni(II), and Cu(II) were purchased from Aldrich, whereas [Mn(H₂O)ₓ]BF₄ was prepared directly from the metal and aqueous tetrafluoroboric acid (HBF₄) (48–50%) under an inert atmosphere as reported for V(II).¹⁰ The aqueous salts of the other metals can also be prepared by the same route. Tetracetatodichromatium¹¹ and barium triflate were prepared as described in the literature.¹² All manipulations were carried out under a dry nitrogen atmosphere using standard Schlenk line techniques.

A. BISTETRAFLUOROBORATE–HEXAKISACETONITRILE METAL(II) {[M(CH₃CN)ₓ]BF₄}₂ (M = Fe, Co, Ni)

This method, which involves preparation of acetonitrile cation salts of tetrafluorooborate from oxidation of metals with NOBF₄, is the one reported in a general manner by Hathaway and co-workers according to the following equation:

\[ M + NOBF_4 + xCH_3CN \rightarrow [M(CH_3CN)_x][BF_4]_2 + NO \]

Procedure

**Caution.** Nitrosonium tetrafluoroborate (NOBF₄) is corrosive and moisture sensitive and should be stored under nitrogen in a freezer.

In a typical reaction, 0.50 g of NOBF₄ (4.32 mmol) and a molar excess of the solid, powdered metal are loaded into a 250-mL round-bottomed flask. Acetonitrile (40 mL) is added to the mixture with stirring and the flask is exposed to vacuum until filled with ~0.847 g (87%)

B. BISTETRABORATE–MANG.

Procedure

Manganese are added to nitrile (40 n a needle out filtered and ~5 mL, after precipitate. discarded. It

C. BISTETRONIUM COPPE
vacuum until the solution begins to bubble vigorously. The system is then back-filled with nitrogen and the process is repeated 3 additional times to remove the liberated NO gas. The flask is then isolated from the vacuum manifold and stirred for 12 h under reduced pressure. The solution volume is reduced under vacuum to ~10 mL (or until cloudy), transferred via cannula to a clean flask, treated with diethyl ether (50 mL) to complete the precipitation, and cooled in an ice bath to allow the solid to settle. The liquid is removed through a cannula, and the solid product is washed with copious amounts of diethyl ether and thoroughly dried under vacuum. Typical yields are 0.658 g (65%) for the white Fe product, 0.897 g (87%) for the pink Co solid, and 0.453 g (42%) for the blue Ni compound.

Slight modifications of this procedure are used to prepare \([\text{Mn(CH}_3\text{CN})_4] (\text{BF}_4)_2\) and \([\text{Cu(CH}_3\text{CN})_4](\text{BF}_4)_2\).

**B. BISTETRAFLUOROBORATE–TETRAKISACETONITRILE MANGANESE(II) \([\text{Mn(CH}_3\text{CN})_4](\text{BF}_4)_2\)**

*Procedure*

Manganese chips (1.60 g, 29.1 mmol, excess) and NOBF\(_4\) (1.64 g, 14.0 mmol) are added to a 250-mL round-bottomed flask under an inert atmosphere. Acetonitrile (40 mL) is added with stirring and the NO(g) is allowed to escape through a needle outlet placed in a septum. After stirring for 20 h, the reaction mixture is filtered and the colorless filtrate is concentrated under a dynamic vacuum to ~5 mL, after which time diethyl ether (40 mL) is added to produce a white precipitate. The supernatant is removed from the solid with a cannula and is discarded. The solid is washed with diethyl ether and dried under vacuum to yield a white crystalline product. A typical yield is 2.09 g (76%).

**C. BISTETRAFLUOROBORATE–TETRAKISACETONITRILE COPPER(II) \([\text{Cu(CH}_3\text{CN})_4](\text{BF}_4)_2\)**

*Procedure*

An amount of NOBF\(_4\) (0.425 g, 3.64 mmol) and a slight molar excess of Cu powder are loaded into a round-bottomed flask no smaller than 250 mL in capacity. Ethyl acetate (30 mL) is added to the mixture with stirring, and the flask is exposed to a vacuum until the solution begins to bubble vigorously. The flask is then backfilled with inert gas and the vacuum is again briefly applied. This
process is repeated 3 additional times to remove NO gas, after which time the flask is isolated from the vacuum manifold and stirred for 12 h under reduced pressure. The blue solution is reduced to 10 mL (or until saturated), transferred via cannula to a separate flask, and treated with acetonitrile (30 mL) to precipitate the desired pale blue product. The mixture is then cooled in an ice bath to settle out the product. The solid product is finally washed with copious amounts of diethylether, dried under vacuum, and stored in a drybox. The yield is 0.584 g (75%). Ethyl acetate is used in the first part of the procedure because direct oxidation of copper metal in acetonitrile leads to a mixture of cuprous [Cu(I)] and cupric [Cu(II)] products. Evidently, ethyl acetate is not a good ligand for stabilizing the cuprous ion in solution.

The remaining procedures presented in this section (syntheses D–H) involve preparation of acetonitrile-solvated cations from the water-solvated cations. The common formula for these compounds is as follows:

$$[M(H_2O)_x]_2(BF_4)_2 + CH_3CN \xrightarrow[\Delta, sieve, \text{in H}_2O]{} [M(CH_3CN)_x][(BF_4)_2]$$

D. [M(CH_3CN)_x][(BF_4)_2] FROM [M(H_2O)_x][(BF_4)_2] (M = Mn, Fe, Co, Ni, Cu)

**Procedure**

**Caution.** The fluoroboric acid aquo complex (HBF₄) is corrosive and a lachrymator. Triethylxonium tetrafluoroborate, [(Et₂O)(BF₄)] is toxic, corrosive, a neurologic hazard, a suspected carcinogen, and moisture-sensitive and should be stored under nitrogen in a freezer.

This method involves the exchange of the H₂O ligand for CH₃CN and subsequent removal of the water from the acetonitrile solution. This method has been used with the Mn(II), Fe(II), Co(II), Ni(II), and Cu(II) solvated cations.

Amounts of [M(H₂O)ₓ](BF₄)₂ in the range of 3–5 g are transferred to a 250-mL Schlenk flask in a nitrogen-purged glovebag. The Schlenk flask is fitted with a Soxhlet extractor (3-cm-diameter 15-cm-high column) that has been loaded with 3-Å molecular sieves, and dry acetonitrile (~120 mL) is added through the top of the extractor to cover the sieves. It is important that sufficient acetonitrile be added to ensure that when the extractor is filled there is acetonitrile remaining in the bottom Schlenk flask. A condenser is added to the top of the extractor and the acetonitrile solution is refluxed and extracted through the sieves for 4–5 days. The mixture is then cooled and filtered to remove any insoluble materials. The solution is then concentrated under vacuum, diethyl ether is added to precipitate the product, and the solvent is removed with the use of a car and dried thor 3.73 g (85%) t 91% for Cu.

If larger quenches of fresh detected in the t the solids in dry

E. BISTETRAG CHROMIUM ACETATE

**Procedure**

Because of its ex- parred by an altera- tion of C 13 mL (13 mmo tion is allowed t green precipitate carded. The vol 10–15 mL and blue product. (S solution is rem CH₂Cl₂ (20 mL) der and transferr

F. PREPARAT TRIFLUORO

In applications for nate (trflate) co (CF₃SO₃)⁻ is me plays high therm cationic clusters spectrometric an:

**Procedure**

All glassware is | dried in an over
the use of a cannula. The solid is washed with copious amounts of diethyl ether and dried thoroughly under vacuum. Typical yields are 3.34 g (91%) for Mn, 3.73 g (85%) for Fe, 4.33 g (87%) for Co, 3.96 g (88%) for Ni, and 3.47 g (91%) for Cu.

If larger quantities of the water precursors are used, one must use multiple batches of freshly activated sieves during the dehydration process. If water is detected in the infrared spectrum of the product, then it is necessary to redissolve the solids in dry acetonitrile and repeat the Soxhlet extraction reflux procedure.

E. BISTETRAFLUOROBORATE–TETRAKISACETONITRILE CHROMIUM(II) [Cr(CH₃CN)₄(BF₄)₂ FROM CHROMOUS ACETATE [Cr₂(O₂CCH₃)₄]

Procedure

Because of its extreme sensitivity, it is recommended that the Cr complex be prepared by an alternative method to the two outlined above.¹³ To a stirring suspension of 1 g of Cr₂(O₂CCH₃)₄ (2.94 mmol) in acetonitrile (50–60 mL) is added 13 mL (13 mmol, 4.4 equiv) of a 1 M CH₂Cl₂ solution of (Et₃O)(BF₄). The reaction is allowed to stir overnight to give a blue solution and a small quantity of green precipitate. The blue solution is filtered to remove the solid, which is discarded. The volume of the filtrate is reduced under vacuum to approximately 10–15 mL and two portions of CH₂Cl₂ (20 mL) are added to precipitate the blue product. (Slow and careful addition of CH₂Cl₂ can produce crystals.) The solution is removed from the solid with a cannula and the product is washed with CH₂Cl₂ (20 mL). The solid is then dried under vacuum to give a light blue powder and transferred for storage into the drybox. A typical yield is 1.13 g (49%).

F. PREPARATION OF ACETONITRILE CATIONS WITH TRIFLUOROMETHANESULFONATE (TRIFLATE) ANIONS

In applications for which greater solubility is desired the trifluoromethanesulfonate (triflate) counterion is a better choice than tetrafluoroborate. Although (CF₃SO₂)⁻ is more highly coordinating than (BF₄)⁻, it is quite labile and displays high thermal stability. Triflate salts are used widely as anions for highly cationic clusters in order to increase their solubility and volatility for mass spectrometric analysis.¹⁴–¹⁶

Procedure

All glassware is pretreated with the commercially available reagent glassclad,¹⁷ dried in an oven at 125°C for at least one hour, and cooled in a vacuum
desiccator over drierite (100% CaSO₄). All compounds are handled in a dry anaerobic atmosphere.

G. ANHYDROUS METAL TRIFLATE COMPLEXES

\[
\text{[M}^2\text{(H}_2\text{O)}_x\text{][SO}_3\text{CF}_3\text{]}_2 \xrightarrow{\Delta} \text{M}^2\text{(SO}_3\text{CF}_3\text{)}_2 (M = \text{Mn,Fe,Co,Ni})
\]

The metal aqua triflate complexes are prepared as previously reported.\textsuperscript{7,12} It was found that drying the solids by rotary evaporation is not sufficient to remove all of the water; therefore the samples should be heated for at least 12 h at \(\sim 90^\circ\text{C}\) under vacuum. Prolonged heating should be avoided, as decomposition of the sample occurs. Extended X-ray absorption fine structure (EXAFS) and vibrational spectral data of anhydrous metal triflates have already been reported and can be used to verify the identity of the products.\textsuperscript{18} The colors of the anhydrous metal triflate complexes are white for Mn, white/off-white for Fe, pink for Co, and yellow for Ni.

H. METAL ACETONITRILE COMPLEX CATIONS WITH TRIFLATE ANIONS

Procedure

Acetonitrile is refluxed over 3-Å molecular sieves and further dried by elution from an activated alumina column.

The anhydrous triflate complex (Mn (1.133 g, 3.21 mmol)–Fe (0.382 g, 1.08 mmol)–Co (0.257 g, 0.720 mmol)–Ni (0.731 g, 2.05 mmol) is added to a dry 250-mL round-bottomed Schlenk flask and treated with \(\sim 150\) mL of acetonitrile for 12 h. The volume of the solution is reduced to \(\sim 5\) mL under vacuum and the product is precipitated by the addition of diethyl ether (40 mL). The solution is removed via cannula, and the solid is dried under vacuum, redissolved in 20 mL acetonitrile, and finally filtered through a medium-porosity Schlenk frit to remove minor decomposition products carried over from the \(\text{M(O}_2\text{SCF}_3\text{)}_2\) precursors. The solution is reduced to \(\sim 5\) mL under vacuum and precipitated by the addition of \(\sim 40\) mL of diethyl ether. The colors and typical yields are 0.917 g (55%) for the white Mn product, 0.326 g (50%) for a white/off-white Fe product, 0.255 g (59%) for a pink-peach Co solid, and 0.873 g (71%) for a blue Ni compound. The products are exceedingly moisture-sensitive.

<table>
<thead>
<tr>
<th>TABLE I. UV-Vis</th>
<th>M\textsuperscript{II}</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crz</td>
<td>blue</td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>white</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>white</td>
<td></td>
</tr>
<tr>
<td>Co</td>
<td>pink</td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>blue</td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>blue</td>
<td></td>
</tr>
</tbody>
</table>

- Infrared: Samples were measured on a Magna 560spectrometer.
- Magnetic susceptibility: \(\chi\) \(=\) \(10\) cm\(^3\) mol\(^{-1}\) K\(^{-1}\) for each compound.
- UV-Visible: Concentrations were measured at 374 mM acetonitrile solvent.
General Properties of Metal Reagents

1. Tetrafluoroborate Salts. \([\text{Cr(CH}_3\text{CN})_4][\text{BF}_4]_2\) is extremely air/moisture-sensitive. The Mn, Fe, Co, Ni, and Cu derivatives are moisture-sensitive. Accordingly, all of these compounds should be stored and handled only under an inert atmosphere. The salts are soluble in coordinating solvents such as methanol, ethanol, nitriles, acetone, nitromethane, and tetrahydrofuran, and are insoluble in essentially all other solvents. The infrared spectra display (CN bands in the 2200–2300 cm\(^{-1}\)) region typical of coordinated acetonitrile. The electronic spectra exhibit the expected \(d \rightarrow d\) transitions and the room-temperature (RT) effective magnetic moments are typical for high-spin 3d metal complexes. The spin-only values are exceeded in the cases of Co(II) and Fe(II) as expected as a result of to spin–orbit coupling. Infrared, magnetic susceptibility, and electronic spectral data are summarized in Table I.

2. Triflate Salts. The anhydrous triflate complexes are exceedingly moisture-sensitive; thus special care must be taken during transfer and storage. If the salts are exposed to moist ambient air, they will revert to the aqueous complexes in several hours. Infrared spectra of \([\text{M(CH}_3\text{CN})_4\text{X}]_2(\text{SO}_3\text{CF}_3)_2\) salts measured as Nujol mulls exhibit two sharp CN vibrations of approximately equal intensity. The electronic spectra of the \([\text{M(CH}_3\text{CN})_4\text{X}]_2(\text{SO}_3\text{CF}_3)_2\) compounds are similar

<table>
<thead>
<tr>
<th>(\text{M}^{II})</th>
<th>Color</th>
<th>(\nu_{\text{CN}}) (cm(^{-1}))</th>
<th>(\mu_{\text{eff}}) (B.M.)</th>
<th>(\lambda_{\text{max}}) (nm)</th>
<th>(\varepsilon) (M(^{-1}) cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crz</td>
<td>blue</td>
<td>2333 (s), 2305 (s)</td>
<td>3.84</td>
<td>643</td>
<td>10.3</td>
</tr>
<tr>
<td>Mn</td>
<td>white</td>
<td>2312 (m), 2284 (m)</td>
<td>5.81</td>
<td>536</td>
<td>0.3</td>
</tr>
<tr>
<td>Fe</td>
<td>white</td>
<td>2310 (m), 2287 (m)</td>
<td>5.30</td>
<td>912</td>
<td>2.8</td>
</tr>
<tr>
<td>Co</td>
<td>pink</td>
<td>2316 (m), 2292 (m)</td>
<td>5.00</td>
<td>492</td>
<td>11.3</td>
</tr>
<tr>
<td>Ni</td>
<td>blue</td>
<td>2316 (m), 2292 (m)</td>
<td>2.93</td>
<td>958</td>
<td>3.1</td>
</tr>
<tr>
<td>Cu</td>
<td>blue</td>
<td>2322 (m), 2300 (m)</td>
<td>1.83</td>
<td>744</td>
<td>10.8</td>
</tr>
</tbody>
</table>

- Infrared: Samples were prepared as nujol mulls placed between KBr plates.
- Magnetic susceptibility: Measurements were recorded on a Squid susceptometer at 298 K.
- UV-Visible: Concentrations from 30–24 mM in acetonitrile were used for Cr, Fe, Co, Ni, and Cu; 374 mM acetonitrile solutions were used for Mn; path length of 1 cm; background was solvent vs solvent.
TABLE II. UV-Visible, Magnetic Susceptibility and Infrared Data for 
\([M(CH_3CN)_2][SO_2CF_3]_2\) [M = Mn (x = 4); Fe, Co, Ni (x = 6)]

<table>
<thead>
<tr>
<th>$M^{II}$</th>
<th>Color</th>
<th>$\nu_{CN}$ (cm$^{-1}$)</th>
<th>$\nu_{SO}$ (cm$^{-1}$)</th>
<th>$\zeta$ (B.M.)</th>
<th>$\lambda_{max}$ (nm)</th>
<th>$\epsilon$ (M$^{-1}$cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn</td>
<td>white</td>
<td>2311(s)</td>
<td>1043(s)</td>
<td>6.1</td>
<td>unresolvable</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>2281(s)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>white</td>
<td>2314(s)</td>
<td>1039(s)</td>
<td>5.8</td>
<td>904</td>
<td>4.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2285(s)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co</td>
<td>pink</td>
<td>2320(s)</td>
<td>1039(s)</td>
<td>4.0</td>
<td>413</td>
<td>4.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2293(s)</td>
<td></td>
<td></td>
<td>491</td>
<td>19.8</td>
</tr>
<tr>
<td>Ni</td>
<td>blue</td>
<td>2326(s)</td>
<td>1032(s)</td>
<td>3.3</td>
<td>499</td>
<td>7.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2299(s)</td>
<td></td>
<td></td>
<td>572</td>
<td>9.2</td>
</tr>
</tbody>
</table>

- Infrared: Samples were prepared as nujol mulls placed between KBr plates.
- Magnetic susceptibility: Measurements were recorded on a SQUID susceptometer at 298 K.
- UV-Visible: Concentrations from 15-42 mM in acetonitrile were used for Fe, Co, Ni, and Mn: path length of 1 cm; background was solvent vs solvent.

to the tetrafluoroborate salts and are in accord with divalent metal ions in weak to
moderate ligand field environments.$^{19}$ The RT effective magnetic moments for
the products are consistent with the spin-only values for isolated M(II) ions.
Co(II) and Fe(II) have higher RT effective magnetic moments because of spin–
orbit coupling. Magnetic susceptibility and infrared and electronic spectral data
are summarized in Table II.

**Sample Elemental Analyses.** Calcd. for $\text{MnN}_4\text{C}_8\text{H}_{12}\text{B}_2\text{F}_6$: C, 24.46%; H, 3.08%;
N, 14.27%. Found: C, 24.27%; H, 3.13%; N, 14.03%. Calcd. for $\text{CuN}_4\text{C}_8\text{H}_{12}\text{B}_2$
$\text{F}_6$: C, 23.94%; H, 3.01%; N, 13.96%. Found: C, 23.77%; H, 2.96%; N, 13.85%.

**References and Notes**

(1996).
(1986).
12. Synthesis of $[\text{M}^{II}(\text{NCMe})_6]_2^{2+}$ ($\text{M} = \text{V}, \text{Cr}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}$) Salts

19. The Mn sample did not exhibit any observable transitions even at very high concentrations in a 1-cm-pathlength cell. Typically 5-cm-pathlength cells are required to measure the very weak transitions associated with Mn(II) ions.

12. SYNTHESIS OF $[\text{M}^{II}(\text{NCMe})_6]_2^{2+}$ ($\text{M} = \text{V}, \text{Cr}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}$)

SALTS OF TETRA[3,5-BIS(TRIFLUOROMETHYL)PHENYL]BORATE

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Checked by KRISTIN BOWMAN-JAMES and CYNTHIA. N. MILLER†

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 inorganic and materials chemistry. Anions such as ($\text{CF}_3\text{SO}_3$)$^-$ and ($\text{BF}_4$)$^-$ require moderately strong Lewis bases (i. e., MeCN, NH$_3$) to displace them from the coordination sphere of a metal ion. Other nominally inert anions such as ($\text{BPH}_4$)$^-$ can react with a metal center. The solubility of these salts is limited to more coordinating solvents such as MeCN and is generally much less in THF. Tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (TFPB)$^-2$ avoids these limitations as it is essentially noncoordinating and redox-stable between $\sim 1.6$ and $-1.8$ V versus Ag/AgCl(aq). Its salts are extremely soluble (even in diethyl ether) and can be prepared with many different cations, including Na$^+$, Ag$^+$, Tl$^+$, [tetraalkylammonium]$^+$.

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and ferrocenium.\textsuperscript{7} The complex \([M^{II}(NCMe)_6](TFPB)_2\) (\(M = V, Cr, Mn, Fe, Co, Ni\)), because of its facile ability to lose MeCN, provides metal cation sources that are soluble in MeCN, THF, and Et\(_2\)O.\textsuperscript{8} Preparation of \([M^{II}(NCMe)_6](TFPB)_2\) (\(M = Mn, Fe, Co, Ni\)) is achieved by anion exchange between the metal dihalide and Ag(TFPB). A nonaqueous preparation of the Ag(TFPB) is included that avoids the tedious light-sensitive extraction and drying that existing aqueous routes require.\textsuperscript{5} When \(M = Cr\) and \(V\), the silver salts back-react (oxidize) the divalent metal ions, thereby requiring a different strategy based on nonaqueous \(V^{II}\) and \(Cr^{II}\) precursors. Reliable and convenient nonaqueous routes to \([V^{II}(NCMe)_6][BPh_4]_2\) are also presented. In another contribution to this volume the preparation of \([Cr^{II}(NCMe)_4][BF_4]_2\) is reported.\textsuperscript{9}

\textbf{Materials and General Procedures}

All manipulations are performed under nitrogen or argon using standard Schlenk techniques or in a Vacuum Atmospheres inert-atmosphere DriLab enclosure. Dichloromethane is dried and distilled under \(N_2\) from CaH\(_2\). Acetonitrile is dried and twice distilled under \(N_2\) from CaH\(_2\). Diethylether and tetrahydrofuran are dried and distilled under \(N_2\) from sodium benzophenone ketyl radical. Ag(CF\(_3\)SO\(_3\))\(_2\), [(Ph\(_3\)P)_2N]Cl (Aldrich), AgNO\(_3\) (Alfa), MnCl\(_2\) (Allied Chemical, anhydrous, 99%), NiBr\(_2\), CoCl\(_2\), and FeBr\(_2\) (Mallinckrodt, anhydrous, 99%) are used as received. VCl\(_3\)(MeCN)\(_3\) is prepared by the literature procedure.\textsuperscript{11} [(Ph\(_3\)P)_2N][TFPB] is obtained by mixing together dichloromethane solutions containing stoichiometric amounts of [(Ph\(_3\)P)_2N]Cl and K(TFPB), filtering off the KCl byproduct, and removing the dichloromethane under reduced pressure leaving a white solid.\textsuperscript{•}

The preparation of \([V(NCMe)_6][BPh_4]_2\) is based on a published procedure\textsuperscript{10} with only slight modifications as follows. A solution of VCl\(_3\)(MeCN)\(_3\) (0.749 g, 2.67 mmol) in 85 mL of MeCN is added to a 125-mL Erlenmeyer flask containing NaBPh\(_4\) (2.79 g, 8.14 mmol). This green solution is stirred at room temperature for 2 h, concentrated under reduced pressure to \(\sim 60\) mL, and left at room temperature for 3 weeks to give a mixture of blue-green prisms of \([V(NCMe)_6][BPh_4]_2\) and colorless NaCl. This mixture is filtered and the solid (\(\sim 2.3\) g) stirred in 60 mL of MeCN, the undissolved NaCl (\(\sim 0.130\) g) filtered off, and the blue solution cooled to \(-40^\circ\)C to recrystallize 2.05 g (82% yield) of blue-green prisms in 2 days. IR (Nujol): 2310(m), 2281(m) cm\(^{-1}\).

\textsuperscript{•} It should be noted that the checkers obtained \(\sim 10\)\% lower yields for the \([M^{II}(NCMe)_6][TFPB]_2\) (\(M = V, Cr, Mn, Fe, Co, Ni\)) complexes.
A. POTASSIUM TETRA-3,5-BIS(TRIFLUOROMETHYL)PHENYLBORATE, (K[B(C₆H₃(CF₃)₂]₄))

\[
\text{Mg} + \text{C}_6\text{H}_3\text{I(CF}_3\text{)}_2 \rightarrow \text{Mgl[C}_6\text{H}_3\text{(CF}_3\text{)}_2] \\
8\text{Mgl[C}_6\text{H}_3\text{(CF}_3\text{)}_2] + 2\text{BF}_3 \rightarrow \text{Mg{B[C}_6\text{H}_3\text{(CF}_3\text{)}_2]₄} + 3\text{MgF}_2 + 4\text{Mgl}_2 \\
\text{K}_2\text{CO}_3 + \text{Mg{B[C}_6\text{H}_3\text{(CF}_3\text{)}_2]₄} \rightarrow \text{K{B[C}_6\text{H}_3\text{(CF}_3\text{)}_2]₄} + \text{MgCO}_3
\]

A flame-dried 200-mL round-bottomed flask equipped with a reflux condenser, addition funnel, stir bar, and Mg turnings (0.824 g, 33.9 mmol) is evacuated and backfilled with N₂ 3 times and charged with 10 mL Et₂O. A 20-mL Et₂O solution of 3,5-(trifluoromethyl)iodobenzene (3.84 g, 11.3 mmol) is added dropwise over ~30 min with stirring and the reaction mixture turns green-brown. After stirring for 1 h a 5-mL Et₂O solution of BF₃·Et₂O (0.320 g, 2.26 mmol) is added dropwise over ~30 min with stirring. The reaction mixture is refluxed overnight, after which, it is poured portionwise into a 500-mL Erlenmeyer flask containing a stirring solution of K₂CO₃ (25 g in 100 mL H₂O) to generate the potassium salt. The MgCO₃ precipitate is filtered off and washed 4 times with 25 mL of Et₂O. The Et₂O layer is removed and the aqueous layer saturated with KCl and, in a 250-mL separatory funnel, extracted 4 times with 25 mL of Et₂O. The combined Et₂O layers are concentrated to dryness under reduced pressure, leaving an orange residue. The residue (~2 g) is redissolved in 20 mL CH₂Cl₂/THF (1 : 1) and layered with 20-mL hexane portions to recrystallize the product in 4 days. The product is recrystallized a second time in the same manner to give colorless prisms (1.77 g, 87%) that become opaque when dried in vacuo due to solvent loss. This compound is stable at room temperature indefinitely. (dp: >300°C). IR (Nujol): 1615(w), 1360(m), 1285(s), 1143(s), 1084(m). NMR: \(^1H\) (CD₂Cl₂): 7.74 (m, o, 8H), 7.58 (m, p, 4H) ppm. \(^19F\) (CD₂Cl₂): 99.77 (s) ppm relative C₆F₆.†

Anal. Calcd. for BC₃F₂₄H₂₁K: C, 42.61, H, 1.34. Found: C, 42.98; H, 1.52.

† Yields can be increased (from 48.4 to 71.8%) when the reaction is allowed to reflux for 24–30 h with a dry-ice condenser according to a checker of this synthesis.

† Layering the ether solution with hexane each day for 3 days at freezer temperatures was a preferred method of crystallization for a checker of this synthesis.

† This value was observed by a checker at-134.233 ppm relative to CFCl₃.
B. SILVER TETRA-3,5-BIS(TRIFLUOROMETHYL) PHENYLBORATE (Ag[B[C₆H₃(CF₃)₂]₄])

\[
\text{AgNO}_3 + K\{B[C_6H_3(CF_3)_2]_4\} \rightarrow \text{Ag}\{B[C_6H_3(CF_3)_2]_4\} + \text{KNO}_3
\]

Ag\{B[C₆H₃(CF₃)₂]₄\} is prepared by adding a dry 7-mL MeCN solution of Ag(NO₃) (1.086 mmol, 0.1846 g) to a 10-mL MeCN solution of K\{B[C₆H₃(CF₃)₂]₄\} (1.109 mmol, 1.000 g) in a 50-mL Erlenmeyer flask. After stirring for 10 min, 10 mL of Et₂O is added to help precipitate KNO₃, which is removed by filtration. The filtrate is concentrated under reduced pressure to dryness (without heating above ~80°C). The white residue is dissolved in 25 mL of THF while minimizing light exposure and the remaining KNO₃ removed by filtration. The filtrate is layered with 40 mL of hexane and kept at −30°C to crystallize the product. Colorless prisms (0.834 g, 79% yield) that become slightly cloudy when dried in vacuo are recovered after 7 days. This compound is stable for several months when stored cold in darkness. IR (Nujol): 1609(m), 1357(s), 1281(vs), 1144(vs), 1124(vs) cm⁻¹. TGA: 87.8% weight loss between 122°C (15°C/min) and 250°C leaving a white residue; calculated 86.9% weight loss for AgF as residue. NMR: \(^1\)H (CD₂Cl₂): 7.77 (m, o, 8H), 7.62 (m, p, 4H) ppm. \(^{19}\)F (CD₂Cl₂): 99.77(s) ppm relative C₆F₆.

Anal. Calcd. for the 0.28 hexane solvate AgBC₃₃.₆₅H₁₄.₂₄F₂₄: C, 40.65; H, 1.61. Found: C, 40.55; H, 1.84.

C. HEXAKIS(ACETONITRILE)MANGANESE(II)BIS-TETRA-3,5-BIS(TRIFLUOROMETHYL)PHENYLBORATE ([Mn\(^{II}\)(NCMe)₆]{B[C₆H₃(CF₃)₂]₄})

\[
\text{MnCl}_2 + 2\text{Ag}\{B[C_6H_3(CF_3)_2]_4\} + 6\text{MeCN} \rightarrow \\
[Mn\(^{II}\)(NCMe)₆]{B[C_6H_3(CF_3)_2]_4} + 2\text{AgCl} + 6\text{MeCN}
\]

A dry 15-mL MeCN solution of Ag\{B[C₆H₃(CF₃)₂]₄\} (1.332 mmol, 1.293 g) is added to MnCl₂ (0.6662 mmol, 0.0838 g) in a 25-mL Erlenmeyer flask, and the mixture is stirred at room temperature in darkness for 12 h. The silver chloride is filtered off, leaving a pale pink solution. This is concentrated under reduced pressure to ~6 mL and cooled to −40°C for 24 h to crystallize colorless needles that are filtered cold (>80% yield) and stored at −40°C. IR (Nujol): 2315(m), 2289(m) cm⁻¹. TGA (thermogravimetric analysis) weight loss between room temperature and 450°C (15°C/min): 84.2%.

Anal. Calcd. H, 2.00; 1

D. HEXAKIS(BIS(T)

\[
\text{FeBr}_2 + 2
\]

A dry 15-mL mixture is filtered under pressure to that are filtrated 2291(m) cm⁻¹: 84.4

Anal. Calc. 1.88; N, 4.

E. HEXAKIS(ACETONITRILE)MANGANESE(II)BIS-TETRA-3,5-BIS(TRIFLUOROMETHYL)PHENYLBORATE ([Co\(^{II}\)\])

\[
\text{CoCl}_2 + 2
\]

A dry 15-mL mixture is filtered off, to ~6 mL of filtered cold cm⁻¹. TG, 85.5%.
12.  Synthesis of \([M^{II}(NCMe)_6]_2^{2+} \text{ (} M = V, Cr, Mn, Fe, Co, Ni \text{)} \) Salts

**D. HEXAKIS(ACETONITRILE)IRON(II)BIS-TETRA-3,5-BIS(TRIFLUOROMETHYL)PHENYLBORATE**

\([\text{Fe}^{II}(NCMe)_6][\text{B}[C_6H_3(CF_3)_2]_4]_2\)

\[
\text{FeBr}_2 + 2\text{Ag}\{\text{B}[C_6H_3(CF_3)_2]_4\} + 6\text{MeCN} \rightarrow
\]

\[\text{[Fe}^{II}(NCMe)_6]\{\text{B}[C_6H_3(CF_3)_2]_4\}_2 + 2\text{AgBr}\]

A dry 15-mL MeCN solution of Ag\{B[C_6H_3(CF_3)_2]_4\} (1.332 mmol, 1.293 g) is added to FeBr_2 (0.6662 mmol, 0.1437 g) in a 25-mL Erlenmeyer flask and the mixture is stirred at room temperature in darkness for 12 h. The silver bromide is filtered off, leaving a pale yellow solution. This is concentrated under reduced pressure to ~6 mL and cooled to -40°C for 24 h to crystallize colorless needles that are filtered cold (> 80% yield) and stored at -40°C. IR (Nujol): 2318 (m), 2291 (m) cm\(^{-1}\). TGA weight loss between room temperature and 450°C (15°C/min): 84.4%.

**Anal.** Calcd. B_2C_{76}F_{48}H_{42}MnN_6: C, 45.02; H, 2.09; N, 4.14. Found: C, 45.29; H, 2.00; N, 4.57.

**E. HEXAKIS(ACETONITRILE)COBALT(II)BIS-TETRA-3,5-BIS(TRIFLUOROMETHYL)PHENYLBORATE**

\([\text{Co}^{II}(NCMe)_6][\text{B}[C_6H_3(CF_3)_2]_4]\)

\[
\text{CoCl}_2 + 2\text{Ag}\{\text{B}[C_6H_3(CF_3)_2]_4\} + 6\text{MeCN} \rightarrow
\]

\[\text{[Co}^{II}(NCMe)_6]\{\text{B}[C_6H_3(CF_3)_2]_4\}_2 + 2\text{AgCl}\]

A dry 15-mL MeCN solution of Ag\{B[C_6H_3(CF_3)_2]_4\} (1.332 mmol, 1.293 g) is added to CoCl_2 (0.6662 mmol, 0.0865 g) in a 25-mL Erlenmeyer flask and the mixture is stirred at room temperature in darkness for 12 h. The silver chloride is filtered off, leaving a pink solution. This is concentrated under reduced pressure to ~6 mL and cooled to -40°C for 24 h to crystallize pale pink needles that are filtered cold (> 80% yield) and stored at -40°C. IR (Nujol): 2321 (m), 2295 (m) cm\(^{-1}\). TGA weight loss between room temperature and 450°C (15°C/min): 85.5%.
F. HEXAKIS(ACETONITRILE)NICKEL(II)BIS-TETRA-3,5-BIS(TRIFLUOROMETHYL)PHENYLBORATE
([NiII(NCMe)6][B[C6H3(CF3)2]4])

NiBr2 + 2Ag{B[C6H3(CF3)2]4} + 6MeCN →

[NIII(NCMe)6]{B[C6H3(CF3)2]4}2 + 2AgBr

A dry 15-mL MeCN solution of Ag{B[C6H3(CF3)2]4} (1.332 mmol, 1.293 g) is added to NiBr2 (0.6662 mmol, 0.456 g) in a 25-mL Erlenmeyer flask and the mixture is stirred at room temperature in darkness for 12 h. The silver bromide is filtered off, leaving a sky-blue solution. This is concentrated under reduced pressure to ~6 mL and cooled to -40°C for 24 h to crystallize blue-purple needles of the product that are filtered cold (> 80% yield) and stored at -40°C. IR (Nujol): 2326(m), 2299(m) cm⁻¹. TGA weight loss between room temperature and 450°C (15°C/min): 95.1%.

Anal. Calcd. for B2C76F48H42N6: C, 44.94; H, 2.08; N, 4.14. Found: C, 44.87; H, 2.14; N, 4.89.

G. HEXAKIS(ACETONITRILE)CHROMIUM(II)BIS-TETRA-3,5-BIS(TRIFLUOROMETHYL)PHENYLBORATE
([CrII(NCMe)6][B[C6H3(CF3)2]4]2)

[Cr(NCMe)4](BF4)2 + 2K{B[C6H3(CF3)2]4} + 2MeCN →

[CrII(NCMe)6]{B[C6H3(CF3)2]4}2 + 2K[BF4]

A dry 5-mL THF solution of K{B[C6H3(CF3)2]4} (0.9880 mmol, 0.8913 g) is added to a 6-mL THF/MeCN (5 : 1) solution/suspension of [Cr(NCMe)4](BF4)2 (0.4940 mmol, 0.1926 g) in a 25-mL Erlenmeyer flask. The remaining [Cr(NCMe)4](BF4)2 solid dissolves on addition, and a white precipitate of K[BF4] forms. The reaction mixture is stirred for 4 h at room temperature and then filtered. The filtrate is concentrated under reduced pressure to dryness and the sky-blue solid (~ 1 g) dissolved in 7 mL MeCN to recrystallize the product at -40°C. Recovered 0.742 g (74% yield) of sky-blue needles after 24 h that are...
filtered cold and stored at \(-40^\circ C\). IR (Nujol): 2324(m), 2297(m), 2277(w) cm\(^{-1}\).
TGA weight loss between room temperature and 450°C (15°C/min): 85.1%.

**Anal.** Calcd. for \(\text{B}_2\text{C}_{76}\text{CrF}_{48}\text{H}_{42}\text{N}_6\): C, 45.08; H, 2.09; N, 4.15. Found: C, 45.40; H, 2.28; N, 5.59.

**H. HEXAKIS(ACETONITRILE)VANADIFORM(II)BIS-TETRA-3,5-BIS(TRIFLUOROMETHYL)PHENYLBORATE**
\([\text{V}^\text{II}(\text{NCMe})_6][\text{B}[\text{C}_6\text{H}_5(\text{CF}_3)_2]_4]_2\)

\[\text{[V}^\text{II}(\text{NCMe})_6][\text{B}[\text{C}_6\text{H}_5(\text{CF}_3)_2]_4]_2 + 2[(\text{Ph}_3\text{P})_2\text{N}][\text{B}[\text{C}_6\text{H}_5(\text{CF}_3)_2]_4] \rightarrow \]

\[\text{[V}^\text{II}(\text{NCMe})_6][\text{B}[\text{C}_6\text{H}_5(\text{CF}_3)_2]_4]_2 + 2[(\text{Ph}_3\text{P})_2\text{N}][\text{BPh}_4]\]

A dry 20-mL MeCN/CH\(_2\)Cl\(_2\) (1 : 1) solution of \([(\text{Ph}_3\text{P})_2\text{N}][\text{B}[\text{C}_6\text{H}_5(\text{CF}_3)_2]_4]\) (1.315 mmol, 1.843 g) is added to a stirring 40-mL MeCN solution/suspension of \([\text{V}(\text{NCMe})_6][\text{BPh}_4]\) (0.6413 mmol, 0.6001 g) in a 125-mL Erlenmeyer flask. The remaining solid \([\text{V}(\text{NCMe})_6][\text{BPh}_4]\) dissolves rapidly on addition of the \([(\text{Ph}_3\text{P})_2\text{N}][\text{B}[\text{C}_6\text{H}_5(\text{CF}_3)_2]_4]\) solution and \([(\text{Ph}_3\text{P})_2\text{N}][\text{BPh}_4]\) begins to crystallize. After 20 min the solution is concentrated under reduced pressure to \(\sim 15\) mL and filtered to remove \([(\text{Ph}_3\text{P})_2\text{N}][\text{BPh}_4]\). The blue solution is cooled to \(-40^\circ C\) to crystallize aqua-blue needles mixed with colorless prisms of \([(\text{Ph}_3\text{P})_2\text{N}][\text{BPh}_4]\) in 24 h. The mixture of crystals is isolated by filtration and the \([\text{V}^\text{II}(\text{NCMe})_6][\text{B}[\text{C}_6\text{H}_5(\text{CF}_3)_2]_4]_2\) is dissolved and washed away from the \([(\text{Ph}_3\text{P})_2\text{N}][\text{BPh}_4]\) with 30 mL of Et\(_2\)O. The Et\(_2\)O is removed under reduced pressure and the remaining solid (\(\sim 1\) g) is recrystallized from 7 mL of MeCN at \(-40^\circ C\). Recovered 0.888 g (68% yield) aqua-blue needles in 24 h are filtered cold and stored at \(-40^\circ C\). IR (Nujol): 2320(m), 2291(m) cm\(^{-1}\). TGA weight loss between room temperature and 450°C (15°C/min): 74.3%.

**Anal.** Calcd. for \(\text{B}_2\text{C}_{76}\text{F}_{48}\text{H}_{42}\text{N}_6\text{V}\): C, 45.11; H, 2.09; N, 4.15. Found: C, 44.49; H, 2.06; N, 4.25.

**General Properties**

The \([\text{M}^\text{II}(\text{NCMe})_6][\text{B}[\text{C}_6\text{H}_5(\text{CF}_3)_2]_4]_2\) (\(\text{M} = \text{V}, \text{Cr}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}\)) complexes are moderately moisture-sensitive crystalline solids and the \(\text{V}^\text{II}\) and \(\text{Cr}^\text{II}\) complexes are \(\text{O}_2\)-sensitive. Significant solvent loss from the solid complexes occurs at room temperature within hours, but the complexes are stable for months when stored cold. All the complexes are soluble in coordinating organic solvents (e. g., acetonitrile, THF, diethyl ether). IR spectra, TGA, and magnetic susceptibility (Table I) can be used to identify the complexes in the solid state while UV–vis spectroscopy (Table I) best shows the purity of the metal center. The
### TABLE I. Magnetic and UV–Visible Data for [M\textsuperscript{II} (NCMe)\textsubscript{6}][B\textsubscript{8}H\textsubscript{3} (CF\textsubscript{3})\textsubscript{2}]\textsubscript{4}\textsubscript{2} (M = V, Cr, Mn, Fe, Co, Ni)

<table>
<thead>
<tr>
<th>M\textsuperscript{II}</th>
<th>(\mu_{\text{eff}}^a) m\textsubscript{B}</th>
<th>(\lambda_{\text{max}}, \text{cm}^{-1})</th>
<th>(\varepsilon^b \text{ M}^{-1} \text{ cm}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>V</td>
<td>3.92(1)</td>
<td>16,300</td>
<td>46.3</td>
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<tr>
<td></td>
<td></td>
<td>22,500</td>
<td>46.3</td>
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<tr>
<td>Cr</td>
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<td>9,000</td>
<td>1.8</td>
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<tr>
<td></td>
<td></td>
<td>15,500</td>
<td>12.7</td>
</tr>
<tr>
<td>Mn</td>
<td>5.98(2)</td>
<td>15,100</td>
<td>(\sim 0.2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>19,100</td>
<td>(\sim 0.3)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>23,700</td>
<td>(\sim 0.5)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>26,900</td>
<td>(\sim 0.6)</td>
</tr>
<tr>
<td>Fe</td>
<td>5.85(1)</td>
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<tr>
<td>Ni</td>
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<tr>
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<td>27,500</td>
<td>8.0</td>
</tr>
</tbody>
</table>

\(^a\) 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.

\(^b\) Concentrations were 1–2.5 mM in MeCN, pathlength 5 cm; background was solvent versus solvent; (TFPB)\textsuperscript{−} cutoff above 33,000 cm\(^{-1}\).

IR spectra show two \(\nu_{\text{CN}}\) bands of approximately equal intensity. In TGA experiments decomposition with loss of MeCN and metal abstraction of fluoride from the anion occurs above 130\(^\circ\)C with the production of other decomposition side-products, leaving dark residues at 450\(^\circ\)C. Obtaining reasonable elemental analyses is problematic because of the ease of solvent loss at room temperature and combustion problems. Nonetheless, the elemental analyses of [M\textsuperscript{II} (NCMe)\textsubscript{6}](TFA)\textsubscript{2} (M = V, Cr, Mn, Fe, Co, Ni) are consistent with the proposed formulation, but insensitive to the metal ion. The room temperature effective moments [M\textsuperscript{II} (NCMe)\textsubscript{6}](TFA)\textsubscript{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\textsuperscript{II}, Fe\textsuperscript{II}, Co\textsuperscript{II}, and Ni\textsuperscript{II}. UV–vis spectra of the complexes in acetonitrile show the expected \(d \rightarrow d\) transitions for these octahedral divalent metal centers.

### References and Notes

4. In comparison, the $E_{1/2}$ for $[\text{BPh}_4]^{-}$ was reported to be $\sim-0.5$ V versus Ag/AgNO$_3$ (MeCN).

13. TRANSITION METAL p-TOLUENESULFONATES

Submitted by STEPHEN M. HOLMES,* SCOTT G. MCKINLEY,∗
and GREGORY S. GIROLAMI∗

Checked by PAUL S. SZALAY and KIM R. DUNBAR†

Binary salts of transition metal cations with weakly coordinating anions are extremely useful starting materials. Perchlorate salts have long been known for many transition metal cations, but these salts are potentially explosive in the presence of organic ligands and solvents. For this reason, researchers have increasingly turned to binary salts with nonoxidizing anions such as hexafluoro phosphate, tetrafluoroborate, tetraarylborate, and trifluromethanesulfonate (triflate). Some drawbacks may be associated with the use of these anions. The PF$_6^-$ and BF$_4^-$ anions have a tendency to hydrolyze in aqueous solution to generate HF, whereas tetraarylborate anions (including fluorinated analogs) have relatively reactive B–C bonds, and the aryl rings can coordinate in a π fashion to metal centers. The triflates$^{5,6}$ are moderately expensive to prepare and occasionally difficult to crystallize.

In the present contribution, we describe the preparation of binary transition metal $p$-toluenesulfonates (tosylates), which have been known$^7$ since the 1870s but have been little used as synthetic starting materials. These salts are relatively inexpensive to prepare, can be isolated in high crystalline yields, and are soluble in many polar solvents. Tosylate salts are typically less soluble than the corresponding triflates, but more soluble than corresponding halide salts.

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Transition metal tosylates have been described for Ti$^{III}$, Cr$^{II}$, Cr$^{III}$, Mn$^{II}$, Fe$^{II,III}$, Co$^{II}$, Ni$^{II,III}$, Cu$^{II}$, and Ru$^{II,III}$, as well as for Sc$^{III}$, Y$^{III}$, and the lanthanides Sm$^{III}$, Gd$^{III}$, Dy$^{III}$, Ho$^{III}$, Er$^{III}$, and Yb$^{III}$. Alkali metal tosylates have also been briefly described for Li, Na, K, and Cs. These compounds are typically prepared by addition of $p$-toluenesulfonic acid to a metal carbonate, hydroxide, or carboxylate, or by addition of silver tosylate to a metal chloride.

In the present contribution, we describe the preparations of several binary transition metal tosylates directly from the metal and $p$-toluenesulfonic acid under an inert atmosphere. This method is easy to carry out, and affords products that are completely free of contaminating counterions. The presence of excess metal provides a reducing environment, so that divalent products are obtained for all first-row transition metals except for Ti and V, which form trivalent products under these reaction conditions. The Cr$^{II}$ salt may be converted to Cr$^{III}$ (OTs)$_3$ by air oxidation in the presence of excess $p$-toluenesulfonic acid. Tosylate salts of Ti$^{III}$, V$^{III}$, Fe$^{III}$, and Cs can also be prepared by treatment of the corresponding metal chloride with $p$-toluenesulfonic acid, and a vanadyl salt has been prepared by similar treatment of vanadyl acetylacetonate.

Methods for preparing anhydrous tosylate salts are also described. Analytical and infrared data for the anhydrous tosylate salts are presented in Tables I and II. The IR spectra of the hydrated salts are essentially identical to those of the anhydrous salts, except extra bands due to water are present near 3150–3500 and 1650–1700 cm$^{-1}$.

Procedure

Except where noted, all procedures were carried out under a dry argon atmosphere using Schlenk and cannula techniques. VO(acac)$_2$ was prepared by

| TABLE I. Analytical Data for the Anhydrous Tosylate Salts$^a$ |
|-----------------|---|---|---|
| Compound        | Color  | C     | H     | M     |
| Ti(OTs)$_3$     | Pale green | 44.9 (44.5) | 3.78 (3.79) | 8.53 (9.13) |
| V(OTs)$_3$      | Pale green | 44.6 (42.4) | 3.76 (4.18) | 9.02 (9.51) |
| VO(OTs)$_2$     | Gray    | 41.0 (40.9) | 3.45 (3.47) | 12.5 (12.4) |
| Cr(OTs)$_2$     | Pale green | 42.6 (41.8) | 3.59 (3.99) | 13.2 (12.0) |
| Mn(OTs)$_2$     | White   | 42.3 (42.1) | 3.56 (3.50) | 13.8 (14.0) |
| Fe(OTs)$_2$     | Buff    | 42.2 (41.9) | 3.55 (3.38) | 14.0 (15.4) |
| Fe(OTs)$_3$     | Orange  | 44.3 (41.8) | 3.72 (3.57) | 9.81 (9.57) |
| Co(OTs)$_2$     | Lavender| 41.9 (41.1) | 3.52 (3.64) | 14.7 (14.5) |
| Ni(OTs)$_2$     | Yellow  | 41.9 (41.7) | 3.53 (3.85) | 14.6 (14.3) |

$^a$ Calculated (found).
TABLE II. Infrared Data for the Hydrated Tosylate Salts$^a$

<table>
<thead>
<tr>
<th>Compound</th>
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$^a$Frequencies in cm$^{-1}$.

a published method.\textsuperscript{22} Ti (Cerac), V (Cerac), Cr (Cerac), Mn (Aesar), Fe (Baker), Co (Fisher), Ni (Allied Chemical), TiCl$_3$ (Cerac), VCl$_3$ (Aldrich), FeCl$_3$ (Cerac), CsCl (Cerac), and \textit{p}-toluenesulfonic acid hydrate (Acros, Aldrich) were used as received. Anhydrous \textit{p}-toluenesulfonic acid was prepared by heating the hydrate to 160°C under vacuum for 1 h. Solvents were dried over CaH$_2$ (acetonitrile), Mg turnings (methanol), or Na/benzophenone (diethylether) under nitrogen. Deionized water was sparged with argon before use.

\textbf{Caution.} \textit{Solid \textit{p}-toluenesulfonic acid and its solutions are corrosive.}

\section*{A. TETRAQUOTITANIUM(III)/TRIS-\textit{p}-TOLUENESULFONATE}

\[ \text{Ti} + 3\text{HOT}_2\cdot\text{H}_2\text{O} + \text{H}_2\text{O} \rightarrow [\text{Ti(OH)}_2]_4(\text{OT})_3 + \frac{3}{2}\text{H}_2 \]

To \(\sim\)325-mesh titanium powder (1.19 g, 24.8 mmol) in a 250-mL, round-bottomed flask equipped with a reflux condenser is added \textit{p}-toluenesulfonic
acid monohydrate (18.96 g, 99.7 mmol) and water (40 mL). The mixture is heated to reflux for 5 h; after this time, some metal powder is still present. The resulting purple solution is filtered while hot through Celite, and the filter cake is washed with water (2 × 50 mL). The purple filtrate is concentrated to 25 mL by vacuum distillation, and then allowed to cool to room temperature. After 2 h, the purple needles that deposit from solution are collected by filtration and dried overnight under vacuum at room temperature. Subsequent crops are obtained by concentrating the mother liquor by vacuum distillation and then cooling the solution to room temperature. Yield: 11.34 g (72.0%).

*Anal.* Calcd. for C$_{21}$H$_{29}$O$_{13}$S$_3$Ti: C, 39.8; H, 4.62; S, 15.2. Found: C, 39.5; H, 5.13; S, 15.8.

*Properties*

Pale purple [Ti(OH)$_2$]$_4$(OT$_3$)$_3$ can be stored indefinitely under an inert atmosphere at room temperature. It is soluble in tetrahydrofuran, methanol, and water, but is insoluble in acetonitrile.

**B. TITANIUM(III)TRIS-p-TOLUENESULFONATE**

$$\text{TiCl}_3 + 3\text{HOTs} \rightarrow \text{Ti(OTs)}_3 + 3\text{HCl}$$

To TiCl$_3$ (1.77 g, 11.5 mmol) in a 250-mL, round-bottomed flask equipped with a reflux condenser is added anhydrous $p$-toluenesulfonic acid (6.20 g, 36.0 mmol). The mixture is heated for 15 min in a bath kept at 160°C, after which time HCl evolution ceases. The mixture is dried for 20 min under vacuum in a bath kept at 160°C, and then cooled to room temperature. The resulting solid is treated with a mixture of acetonitrile (25 mL) and methanol (2 mL) at reflux for 20 min. The resulting purple solution is cooled to room temperature, and a pale green solid precipitates. The solid is collected by filtration, washed with Et$_2$O (2 × 20 mL), and dried overnight under vacuum at room temperature. Additional material can be obtained from the filtrate by concentrating it to 10 mL, adding Et$_2$O (5 mL), and cooling to −20°C. Yield: 4.12 g (67.1%).

*Anal.* Calcd for C$_{21}$H$_{21}$O$_9$S$_3$Ti: C, 44.9; H, 3.78; Ti, 8.53. Found: C, 44.5; H, 3.79; Ti, 9.13.
Properties

Pale green Ti(OTs)$_3$ can be stored indefinitely under an inert atmosphere at room temperature. It is soluble in methanol and water, sparingly soluble in tetrahydrofuran, and insoluble in acetonitrile.

C. HEXAAQUOVANADIUM(III)TRIS-p-TOLUENESULFONATE

$$V + 3\text{HOTs} \cdot \text{H}_2\text{O} + 3\text{H}_2\text{O} \rightarrow [\text{V(OH}_2)_6][\text{OTs}_3] + \frac{3}{2}\text{H}_2$$

To ~325-mesh vanadium powder (3.87 g, 76.0 mmol) in a 250-mL round-bottomed flask equipped with a reflux condenser is added p-toluenesulfonic acid monohydrate (43.3 g, 228 mmol) and water (20 mL). The mixture is heated to reflux for 16 h. A deep purple solution is obtained, and some metal powder is still present. The mixture is filtered while hot through Celite and the purple filtrate concentrated to 10 mL by vacuum distillation. The solution is cooled to room temperature, and large pale purple needles are deposited. The crystals are collected by filtration and dried overnight under vacuum at room temperature. Additional crops can be obtained from the filtrate by concentrating it to 5 mL by vacuum distillation, and then cooling the resulting solution to room temperature. Yield: 23.0 g (45.1%).

Anal. Calcd. for C$_{21}$H$_{33}$O$_{15}$S$_3$V: C, 37.5; H, 4.96; S, 14.3. Found: C, 37.6; H, 5.17; S. 14.2.

Properties

Pale purple [V(OH$_2$)$_6$](OTs)$_3$ can be stored indefinitely under an inert atmosphere at room temperature. It is soluble in methanol and acidified (pH = 2) water. It is sparingly soluble in tetrahydrofuran, and insoluble in acetonitrile. In water at pH 7, the salt is unstable, as shown by the immediate formation of a brown color.

D. VANADIUM(III)TRIS-p-TOLUENESULFONATE

$$\text{VCl}_3 + 3\text{HOTs} \rightarrow \text{V(OTs)}_3 + 3\text{HCl}$$

Anhydrous VCl$_3$ (2.20 g, 13.98 mmol) and anhydrous p-toluenesulfonic acid (7.19 g, 41.75 mmol) are combined in a 250-mL, round-bottomed flask equipped
with a reflux condenser, and the solid mixture is heated for 10 h in a bath kept at 160°C. The mixture is allowed to cool and the resulting pale green solid is washed with Et₂O (30 mL) to remove any remaining acid. The solid is extracted with a boiling 3:1 mixture of acetonitrile and methanol (100 mL). The extract is filtered while still hot, and then was cooled to -20°C overnight. The apple-green plates that form are collected and dried for 16 h under vacuum at room temperature. The filtrate is evaporated to dryness under vacuum at room temperature, and the resulting solid extracted with a refluxing mixture of 10:1 acetonitrile and methanol (10 mL). Cooling the hot extract to room temperature affords additional green material, which is dried as described above. Yield: 7.20 g (91.6%).

Anal. Calcd. for C₂₁H₂₁O₉S₃V: C, 44.6; H, 3.76; N, 0; Cl, 0; V, 9.02. Found: C, 42.4; H, 4.18; N, 0.15; Cl, <0.15; V, 9.51.

Properties
Pale green V(OTs)₃ can be stored indefinitely under an inert atmosphere at room temperature. It is soluble in methanol and acidified (pH = 2) water. It is sparingly soluble in tetrahydrofuran and insoluble in acetonitrile. Anhydrous V(OTs)₃ can also be prepared by dehydration of [V(OH₂)₃](OTs)₃ at 160°C under vacuum (see below).

E. PENTAQUOOXOVANADIUM(IV)BIS-p-TOLUENESULFONATE HEMIHYDRATE

\[ \text{VO(acac)}_2 + 2\text{HOTs} \cdot \text{H}_2\text{O} + \frac{7}{2} \text{H}_2\text{O} \rightarrow [\text{VO(OH}_2)_3]_2(\text{OTs})_2 \cdot 0.5\text{H}_2\text{O} + 2\text{Hacac} \]

Vanadyl acetylacetonate (5.03 g, 19.0 mmol) and p-toluenesulfonic acid monohydrate (7.23 g, 38.0 mmol) are combined as solids in a 250-mL, round-bottomed flask equipped with a reflux condenser. The solids are heated under vacuum for 1 h in a bath kept at 160°C. The mixture is cooled to room temperature, and the resulting green solid extracted with hot H₂O (10 mL). The extract is filtered, and then most of the water is removed by vacuum distillation; a green foam and some viscous green syrup remain. This residue is treated with acetonitrile (20 mL), and the resulting mixture is heated to reflux for 20 min. A large quantity of blue-green plates form on cooling. The crystals are isolated, washed with acetonitrile (20 mL) and Et₂O (20 mL), and dried overnight under vacuum at room temperature. Yield: 8.97 g (94.7%).
Anal. Calcd. for C\textsubscript{14}H\textsubscript{25}O\textsubscript{12.5}S\textsubscript{2}V: C, 33.0; H, 4.97; S, 12.6; V, 10.0. Found: C, 32.9; H, 5.01; S, 12.6; V, 10.0.

**Properties**

Pale green [VO(OH\textsubscript{2})\textsubscript{3}](OTs)\textsubscript{2}·0.5H\textsubscript{2}O can be stored indefinitely at room temperature. It is soluble in methanol and water, but is insoluble in acetonitrile.

**F. TETRAAQUOCHROMIUM(II)BIS-p-TOLUENESULFONATE**

\[
\text{Cr} + 2\text{HOTs} \cdot \text{H}_2\text{O} + 2\text{H}_2\text{O} \rightarrow \left[\text{Cr(OH}_2\right]_4(\text{OTs})_2 + \text{H}_2
\]

To −100/+200-mesh chromium granules (6.0 g, 115 mmol) in a 500-mL, round-bottomed flask equipped with a reflux condenser is added p-toluene sulfonic acid monohydrate (43.26 g, 227 mmol) and water (90 mL). The mixture is heated to reflux for 24 h. A deep blue solution is obtained, and some excess metal powder remains. The hot mixture is filtered through Celite, and the filtrate is allowed to cool to room temperature. The blue needles that form are collected by filtration and dried overnight under vacuum at room temperature. A second crop of crystals is obtained by concentrating the filtrate to ∼20 mL by vacuum distillation and cooling the resulting solution to room temperature. Yield: 45.0 g (84.8%).

Anal. Calcd. for C\textsubscript{14}H\textsubscript{25}O\textsubscript{10}S\textsubscript{2}Cr: C, 36.0; H, 4.76; S, 13.8; Cr, 11.2. Found: C, 34.5; H, 4.77; S, 13.8; Cr, 11.2.

**Properties**

Pale blue [Cr(OH\textsubscript{2})\textsubscript{4}](OTs)\textsubscript{2} can be stored indefinitely under an inert atmosphere at room temperature, but slowly dehydrates to the dihydrate over several months. It is soluble in methanol and water, but is insoluble in acetonitrile.

**G. HEXAQUOCHROMIUM(III)TRIS-p-TOLUENESULFONATE**

\[
\text{Cr} + 3\text{HOTs} \cdot \text{H}_2\text{O} + \frac{1}{4} \text{O}_2 + \frac{5}{2} \text{H}_2\text{O} \rightarrow [\text{Cr(OH}_2\right]_6(\text{OTs})_3 + \text{H}_2
\]

To −100/+200-mesh chromium granules (1.00 g, 19.2 mmol) in a 250-mL, round-bottomed flask equipped with a reflux condenser is added p-toluene sulfonic acid...
monohydrate (11.28 g, 59.3 mmol), and water (40 mL). The mixture is heated to reflux for 3 h, leaving little unreacted metal. The blue mixture is filtered while hot through Celite and the filtrate stirred in air overnight. The dark blue-green solution is concentrated to 25 mL by vacuum distillation. Dry acetonitrile (100 mL) is added, and pale green microcrystals are deposited. The crystals are isolated by filtration, washed with acetonitrile (30 mL) and diethyl ether (60 mL), and dried under vacuum overnight at 25°C. Yield: 11.5 g (88.5%).

**Anal.** Calcd. for C$_{21}$H$_{33}$O$_{15}$S$_3$Cr: C, 35.1; H, 5.34; N, 0.0; S, 13.4; Cr, 7.24. Found: C, 35.5; H, 5.37; N, 0.0; S, 13.2; Cr, 6.58.

**Properties**

Pale green [Cr(OH)$_2$]$6$[(OT)$_3$] can be stored indefinitely at room temperature. It is soluble in methanol and water, but is insoluble in acetonitrile.

**H. TETRAQUOMANGANESE(II)BIS-p-TOLUENESULFONATE HYDRATE**

\[
\text{Mn} + 2\text{HOTs} \cdot \text{H}_2\text{O} + 3\text{H}_2\text{O} \rightarrow [\text{Mn(OH}_2)_4][\text{OTs}_2] \cdot \text{H}_2\text{O} + \text{H}_2
\]

To manganese powder (6.28 g, 114 mmol) in a 250-mL, round-bottomed flask equipped with a reflux condenser is added p-toluenesulfonic acid monohydrate (46.52 g, 245 mmol) and water (150 mL). The mixture is heated to reflux for 1 h. The resulting pale pink solution is filtered through Celite while hot, and the filtrate allowed to cool to room temperature. The deposited white crystals are collected by filtration and dried overnight under vacuum at room temperature. A second crop of white crystals can be obtained by concentrating the mother liquor. Yield: 45.3 g (81.3%).

**Anal.** Calcd. for C$_{14}$H$_{24}$O$_{11}$S$_2$Mn: C, 34.5; H, 4.97; S, 13.2; Mn, 11.3. Found: C, 34.8; H, 4.29; S, 12.1; Mn, 10.8.

**Properties**

White [Mn(OH)$_2$]$4$[(OT)$_3$]$_2$·H$_2$O can be stored indefinitely at room temperature under an inert atmosphere. It is soluble in methanol and water, but is insoluble in acetonitrile and diethylether.

**I. HEXAQUOIRON(II)BIS-p-TOLUENESULFONATE**

\[
\text{Fe} + 2\text{HOTs} \cdot \text{H}_2\text{O} + 4\text{H}_2\text{O} \rightarrow [\text{Fe(OH}_2)_6][\text{OTs}_2] + \text{H}_2
\]

To iron powder equipped v (13.45 g, 7 h. The pale is washed v perature, an filtration an of crystal c (88.5%).

**Anal.** Calcd. H, 5.16; Fe.

**Properties**

Pale green under an inc in acetonitr

**J. IRON(II)**

A mixture of (11.20 g, 58.9 condenser is i orange solid methanol (30 solution is filt of acetonitrile 20 min. The t he orange p obtained from and adding ac diethylether (2 (95.0%).

**Anal.** Calcd. f C, 41.8; H, 3.
To iron powder (4.07 g, 72.9 mmol) in a 250-mL, round-bottomed flask equipped with a reflux condenser is added p-toluenesulfonic acid monohydrate (13.45 g, 70.7 mmol) and water (20 mL). The mixture is heated to reflux for 5 h. The pale green solution is filtered while hot through Celite, and the filter cake is washed with water (3 × 10 mL). The filtrate is allowed to cool to room temperature, and pale green needles form within 2 h. The crystals are collected by filtration and dried overnight under vacuum at room temperature. A second crop of crystal can be obtained by concentrating the mother liquor. Yield: 15.85 g (88.5%).

*Anal.* Calcd. for C_{14}H_{26}O_{12}S_{2}Fe: C, 33.2; H, 5.19; Fe, 11.0. Found: C, 33.7; H, 5.16; Fe, 11.5.

*Properties*

Pale green [Fe(OH)_{6}](OTs)_{2} can be stored indefinitely at room temperature under an inert atmosphere. It is soluble in methanol and water, but is insoluble in acetonitrile and diethyl ether.

**J. IRON(III)TRIS-p-TOLUENESULFONATE**

\[ \text{FeCl}_3 + 3\text{HOTs} \cdot \text{H}_2\text{O} \rightarrow \text{Fe(OTs)}_3 + 3\text{HCl} + 3\text{H}_2\text{O} \]

A mixture of FeCl_{3} (3.18 g, 19.6 mmol) and p-toluenesulfonic acid monohydrate (11.20 g, 58.9 mmol) in a 250-mL, round-bottomed flask equipped with a reflux condenser is heated under vacuum for 1 h in a bath kept at 160°C. The resulting orange solid is washed with diethyl ether (30 mL). The solid is treated with methanol (30 mL), and the mixture heated to reflux for 20 min. The resulting solution is filtered and the filtrate taken to dryness under vacuum. A 3 : 1 mixture of acetonitrile/methanol (30 mL) is added and the mixture heated to reflux for 20 min. The resulting suspension is allowed to cool to room temperature and the orange precipitate is collected by filtration. Additional product can be obtained from the filtrate by concentrating it to 5 mL by vacuum distillation, and adding acetonitrile (10 mL). The orange solids are combined, washed with diethyl ether (20 mL), and dried for 30 min under vacuum at 160°C. Yield: 10.6 g (95.0%).

*Anal.* Calcd. for C_{21}H_{21}O_{9}S_{3}Fe: C, 44.3; H, 3.72; N, 0; S, 16.9; Fe, 9.81. Found: C, 41.8; H, 3.57; N, 0; S, 16.3; Fe, 9.57.
Properties

Orange Fe(OTs)$_3$ can be stored indefinitely at room temperature under an inert atmosphere. It is soluble in methanol and water, and sparingly soluble in tetrahydrofuran. It is insoluble in acetonitrile, diethyl ether, and hydrocarbons.

**K. HEXAQUOCOBALT(II)BIS-p-TOLUENESULFONATE**

\[
\text{Co} + 2\text{HOTs} \cdot \text{H}_2\text{O} + 4\text{H}_2\text{O} \rightarrow [\text{Co(OH}_2)_6][\text{OTs}]_2 + \text{H}_2
\]

To cobalt powder (4.23 g, 71.8 mmol) in a 250-mL, round-bottomed flask equipped with a reflux condenser is added p-toluenesulfonic acid monohydrate (23.26 g, 122 mmol) and water (20 mL). The mixture is heated to reflux for 5 h. The resulting reddish-pink solution is filtered while hot through Celite, and the filter cake is washed with water (3 × 10 mL). The filtrate is cooled to room temperature, and pale orange blocks form after 2 h. The crystals are collected by filtration and dried overnight under vacuum at room temperature. A second crop of crystals are obtained by concentration and cooling of the mother liquor. Yield: 16.75 g (53.8%).

*Anal.* Calcd. for $\text{C}_{14}\text{H}_{26}\text{O}_{12}\text{S}_2\text{Co}$: C, 32.4; H, 5.26; Co, 11.4. Found: C, 32.5; H, 5.05; Co, 10.0.

Properties

Pale orange [Co(OH$_2$)$_6$](OTs)$_2$ can be stored indefinitely at room temperature under an inert atmosphere. It is soluble in methanol and water.

**L. HEXAQUONICKEL(II)BIS-p-TOLUENESULFONATE**

\[
\text{Ni} + 2\text{HOTs} \cdot \text{H}_2\text{O} + 4\text{H}_2\text{O} \rightarrow [\text{Ni(OH}_2)_6](\text{OTs})_2 + \text{H}_2
\]

To nickel powder (5.0 g, 85.2 mmol) in a 250-mL, round-bottomed flask equipped with a reflux condenser is added p-toluenesulfonic acid monohydrate (32.23 g, 169 mmol) and water (20 mL). The mixture is heated to reflux for 15 h; after this time, some metal powder remains. The green mixture is filtered while hot through Celite and the filter cake washed with water (3 × 10 mL). The filtrate is cooled to room temperature, and large green needles deposit on standing. The crystals are collected by filtration and dried overnight under vacuum at room temperature.
room temperature. A second crop of crystals is obtained by concentrating and cooling the mother liquor. Yield: 22.61 g (52.4%).

*Anal.* Calcd. for C_{14}H_{26}O_{12}S_{2}Ni: C, 33.0; H, 4.96; Ni, 11.5. Found: C, 33.2; H, 5.17; Ni, 11.5.

**Properties**

Pale green [Ni(OH)_{6}](OTs)_{2} can be stored indefinitely at room temperature under an inert atmosphere. It is soluble in methanol and water, but is insoluble in acetonitrile and diethyl ether.

**M. CESIUM-p-TOLUENESULFONATE**

\[ \text{CsCl} + \text{HOTs} \cdot \text{H}_{2}\text{O} \rightarrow \text{CsOTs} + \text{HCl} + \text{H}_{2}\text{O} \]

Solid CsCl (5.83 g, 34.6 mmol) and p-toluene sulfonic acid monohydrate (6.60 g, 34.7 mmol) are combined in a 250-mL, round-bottomed flask equipped with a reflux condenser. The mixture is heated for 15 min in a bath kept at 160°C. The resulting yellow slurry solidifies when cooled to room temperature. The solid is treated with methanol (60 mL) and acetonitrile (5 mL), and the mixture is heated to reflux. The solution is filtered while hot, and the pale yellow filtrate is cooled to room temperature. The resulting white plates are isolated by filtration and dried under vacuum at room temperature overnight. A second crop of crystals is obtained by concentrating the mother liquor to 30 mL and adding diethyl ether (30 mL). Yield: 8.01 g (76.1%).

*Anal.* Calcd. for C_{7}H_{7}O_{3}SCs: C, 27.6; H, 2.32; Cl, 0. Found: C, 27.2; H, 2.56; Cl, <0.15.

**Properties**

White Cs(OTs) can be stored indefinitely at room temperature under an inert atmosphere. It is soluble in methanol and water, but is insoluble in acetonitrile and diethyl ether.

**N. PREPARATION OF ANHYDROUS TOSYLATE SALTS**

Anhydrous tosylate salts can be prepared by heating the corresponding hydrated salts under vacuum to 160°C for 1 h. Yields are nearly quantitative. Infrared data for these compounds are shown in Table III.
### TABLE III. Infrared Data for the Anhydrous Tosylate Salts

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\nu(\text{CH})) (w)</th>
<th>Overtone (\nu_a(\text{SO}_2)) (w)</th>
<th>(\nu_a(\text{SO}_2)) (vs)</th>
<th>(\delta(\text{CH})) (vs)</th>
<th>(\delta(\text{CH})) (vs)</th>
<th>(\nu(\text{SO})) (vs)</th>
<th>(\delta(\text{CS}))? (vs)</th>
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<tbody>
<tr>
<td>Ti(O\text{Ts})\text{I}_3</td>
<td>3094</td>
<td>1919</td>
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<td>1149</td>
<td>1040</td>
<td>1010</td>
<td>819</td>
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<tr>
<td></td>
<td>3062</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
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<td>—</td>
</tr>
<tr>
<td>V(O\text{Ts})\text{I}_3</td>
<td>3060</td>
<td>1923</td>
<td>1291</td>
<td>1130</td>
<td>1073</td>
<td>1016</td>
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</tr>
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<td></td>
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<tr>
<td>VO(O\text{Ts})\text{I}_2</td>
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<tr>
<td>Cr(O\text{Ts})\text{I}_2</td>
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<td>1917</td>
<td>1235</td>
<td>1161</td>
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<tr>
<td>Mn(O\text{Ts})\text{I}_2</td>
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<td>Fe(O\text{Ts})\text{I}_2</td>
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<td>1195</td>
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<td>1298</td>
<td>1125</td>
<td>1040</td>
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<tr>
<td>Co(O\text{Ts})\text{I}_2</td>
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<td>1920</td>
<td>1194</td>
<td>1142</td>
<td>1065</td>
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<td>Ni(O\text{Ts})\text{I}_2</td>
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<td>1201</td>
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<tr>
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<td>—</td>
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<td>—</td>
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</tr>
<tr>
<td>Cs(O\text{Ts})</td>
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<td>1940</td>
<td>1223</td>
<td>1128</td>
<td>1037</td>
<td>1015</td>
<td>823</td>
</tr>
</tbody>
</table>

\[^a\text{Frequencies in cm}^{-1}.\]

### Properties

The anhydrous tosylate salts are soluble in methanol and water, but are insoluble in acetonitrile and diethyl ether.

### References

14. SALTS OF BINUCLEAR IRON(II) AND IRON(III) DIANIONS

\([(\text{Fe}_2\text{Cl}_6)^{2-} \text{ AND } (\text{Fe}_2\text{OCl}_6)^{2-}]\)

Submitted by KIM R. DUNBAR,* JOHN J. LONGRIDGE,†
JEREMY M. RAWSON,‡ and JUI-SUI SUN*
Checked by KARL S. HAGEN and BAO DO†

Salts of the oxo-bridged dianion, \((\text{Fe}_2\text{OCl}_6)^{2-}\), particularly its tetra alkyl ammonium derivatives \((\text{R}_4\text{N})_2(\text{Fe}_2\text{OCl}_6)\), have proved to be convenient starting materials for a series of polynuclear iron complexes.\(^1\) The most common procedure utilized for the syntheses of these dinuclear complexes is that described by Armstrong and Lippard,\(^2\) whose yields are significantly greater than those reported in alternative syntheses.\(^3\)

We now report convenient synthetic routes to salts of this binuclear ferric dianion, \((\text{Fe}_2\text{OCl}_6)^{2-}\), and the related binuclear ferrous dianion \((\text{Fe}_2\text{Cl}_6)^{2-}\). Previously we found\(^4\)–\(^6\) that reaction of ferric chloride with phosphines such as tris(2,4,6-trimethoxyphenyl)phosphine (tmpp) unexpectedly yielded the previously unknown \((\text{Fe}_2\text{Cl}_6)^{2-}\) diion as the salt \((\text{Htmpp})_2(\text{Fe}_2\text{Cl}_6)\). Benzene solutions of 
\((\text{Htmpp})_2(\text{Fe}_2\text{Cl}_6)\) reacted\(^7\) with molecular oxygen to yield the phosphine-oxide complex, \(\text{FeCl}_3\) (tmppO), while oxidation in protic solvents such as \(\text{MeOH}\) and \(\text{EtOH}\) formed\(^8\) \((\text{Htmpp})_2(\text{FeCl}_4)\) and \((\text{Htmpp})(\text{FeCl}_4)\) as intermediates, with \(\text{FeCl}_3\) (tmppO) formed only on prolonged oxygenation. We have found that simple salts such as tetraethyl ammonium \([(\text{Et}_4\text{N})^+]\), tetraphenylarsonium

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[(AsPh₄)⁺], tetraphenylphosphonium [(PPh₄)⁺], and bis(triphenylphosphine iminium) [(PPN)⁺] of (Fe₂Cl₆)²⁻ can be conveniently prepared from anhydrous iron(II) chloride and the corresponding chloride salt, such as (Et₄N)Cl, in acetone. In contrast to (Htmp)₂(Fe₂Cl₆), aerial oxidation of these salts proceeds smoothly to form the oxo-bridged binuclear ferric dianion, (Fe₂OCl₆)²⁻. Aerial oxidation of ferrous salts was previously proved to be a convenient route to oxo-bridged ferric complexes; for instance, reaction of FeCl₂·4H₂O with NaOAc yields the trimetallic salt [Fe₃O(OAc)₆]Cl·3H₂O.

Herein we report convenient high-yield routes to both the binuclear ferrous and ferric salts, (PPh₄)₂(Fe₂Cl₆) and (PPh₄)₂(Fe₂OCl₆). These procedures can be readily adapted to other quaternary group 15 cations (R₄N⁺, R₄P⁺, R₄As⁺ and also the iminium cation, PPN⁺). We also report a simple two-step preparation of the (Fe₂OCl₆)²⁻ dianion, which can be carried out on a large scale on the open bench.

The starting materials used in the following syntheses were obtained from commercial sources and used without further purification.

A. DI(TETRAPHENYLPHOSPHONIUM)HEXACHLORODIFERRATE(II) [(Fe₂Cl₆)(PPh₄)₂]

PPh₄Cl + FeCl₂ → (Fe₂Cl₆)(PPh₄)₂

Procedure

A solution of (PPh₄)Cl (0.887 g, 2.367 mmol) in degassed acetone (15 mL) is added to a suspension of FeCl₂ (0.300 g, 2.367 mmol) in degassed acetone (15 mL). The resultant solution is stirred for 12 h to yield a pale yellow precipitate under a yellow solution. The solution is filtered through Celite and the precipitate washed with acetone (20 mL). The combined filtrates are concentrated and Et₂O is added slowly to yield an off-white solid that is dried in vacuo. Yield: 0.854 g, 72%.

Anal. Calcd. for Fe₂Cl₆P₂C₄₈H₄₀ C, 57.5; H, 4.0; Cl, 21.1. Found: C, 57.1; H, 3.9; Cl, 21.0%.

Properties

The IR spectrum of (PPh₄)₂(Fe₂Cl₆) shows a medium–strong νFeCl band at 340 cm⁻¹. The magnetic properties of these salts reveal an interesting dependence on the counterion that is manifested in terms of differences of the Fe–Cl–Fe bridge angles. Full details of the temperature-dependent magnetic
susceptibility measurement of Mössbauer spectra will be the subject of a separate report, although these findings support the existence of ferromagnetic coupling in some of the salts and weak or no coupling between Fe(II) centers in other analogues. For \((\text{PPh}_4)_2(\text{Fe}_2\text{Cl}_6)\), an effective magnetic moment of 7.19\(\mu_B\) at 300 K was observed (using an applied field of 0.1 T).

B. DI(TETRAPHENYLPHOSPHONIUM)(\(\mu\)-OXO)BIS (TRICHLOROFERRATE(III)) \([(\text{PPh}_4)_2(\text{Fe}_2\text{OCl}_6)]\)

Procedure

\[
(\text{PPh}_4)_2(\text{Fe}_2\text{Cl}_6) + \text{O}_2 \rightarrow (\text{PPh}_4)_2(\text{Fe}_2\text{OCl}_6) + \frac{1}{2}\text{O}_2
\]

A solution of \((\text{PPh}_4)_2(\text{Fe}_2\text{Cl}_6)\) (0.119 g, 0.119 mmol) in acetone (20 mL) is purged with \(\text{O}_2\) gas at \(-15^\circ\text{C}\) for 5 min, which results in a color change from yellow to orange after 1 min. The reaction solution is stirred under an \(\text{O}_2\) atmosphere for a further 30 min. The solvent is reduced to a small volume and \(\text{Et}_2\text{O}\) is added to precipitate a yellow solid that is collected by filtration, washed with \(\text{Et}_2\text{O}\), and dried in vacuo. Yield 0.097 g, 80%.

Anal. Calcd. for \(\text{Fe}_2\text{Cl}_6\text{ON}_2\text{Cl}_6\text{H}_14\): C, 32.0; H, 6.7; Cl, 35.4. Found, C, 32.5; H, 7.0; Cl, 35.7%.

Properties

The yellow solid \((\text{PPh}_4)_2(\text{Fe}_2\text{OCl}_6)\) is air-stable in the solid state. The IR spectrum shows broad, strong absorptions at 362 and 874 cm\(^{-1}\) that have been assigned as \(\nu_{\text{FeCl}}\) and \(\nu_{\text{Fe-O-Fe}}\), respectively.

C. DI(TETRAETHYLAMMONIUM)(\(\mu\)-OXO)BIS (TRICHLOROFERRATE(III)) \((\text{Et}_4\text{N})_2(\text{Fe}_2\text{OCl}_6)\)

Procedure

\[
(\text{Et}_4\text{N})\text{Cl} \cdot \text{H}_2\text{O} + \text{FeCl}_2 \cdot 4\text{H}_2\text{O} \rightarrow (\text{Et}_4\text{N})_2(\text{Fe}_2\text{Cl}_6) \cdot 4\text{H}_2\text{O} + \text{H}_2\text{O}
\]

\[
(\text{Et}_4\text{N})_2(\text{Fe}_2\text{Cl}_6) + \text{O}_2 \rightarrow (\text{Et}_4\text{N})_2(\text{Fe}_2\text{OCl}_6) + \frac{1}{2}\text{O}_2
\]
The preparation of this compound is typically carried out with a slight molar excess of FeCl₂·4H₂O as an excess of (Et₄N)Cl has been found² to retard crystallization of the product. It is not necessary to degas solvents for this experiment.

A solution of (Et₄N)Cl·H₂O (1.53 g, 8.33 mmol) in MeOH (10 mL) is added to solution of FeCl₂·4H₂O (1.66 g, 8.33 mmol) in H₂O (10 mL). The solution is stirred for 10 min and the solvent removed in vacuo, yielding a pale yellow solid of composition (Et₄N)₂(Fe₂Cl₄)·4H₂O in quantitative yield. A freshly prepared sample of solid (2.5 g, 3.94 mmol) is dissolved in MeCN (40 mL), and the solution turns an immediate red-brown color. The solution is stirred for 30 min, and filtered to remove a small quantity of insoluble matter, and the filtrate is concentrated to a red-brown oil on a rotary evaporator. Crystals of (Et₄N)₂(Fe₂OCl₆) are recovered from the oily residue using a procedure similar to that reported previously.⁹ The oil is redissolved in MeCN (4 mL) and after addition of THF (30 mL), the solution is cooled to −20°C. After one day the first crop of red-brown crystals are collected by filtration and washed with THF (2 × 10 mL). The combined filtrate and washings are again cooled to −20°C for 24 h to yield a second crop of material, and the procedure is repeated to yield a third crop. The three crops are separately ground to a golden-brown powder and dried in vacuo to remove lattice solvent. The yields for the three crops after drying are 1.365 g (58%), 0.303 g (13%) and 0.094 g (4%), respectively, providing a total yield of 1.762 g (75%).

**Anal.** Calcd. for C₁₆H₄₈N₂Fe₂Cl₆O₄: C, 29.3; H, 7.4; N, 4.3. Found: C, 29.9; H, 7.1; N, 4.3%.

**Anal.** Calcd. for C₁₆H₄₀N₂Fe₂OCl₆: C, 32.0; H, 6.7; N, 4.7. Found: C, 31.9; H, 6.7; N, 4.5%.

**Properties**

Samples of the pale yellow intermediate, (Et₄N)₂(Fe₂Cl₄)·4H₂O, slowly undergo decomposition on exposure to the atmosphere, turning orange, and it is preferable to use a freshly obtained sample for the second step of the reaction presented above. Older samples of this material yield a greater proportion of insoluble material on dissolution in MeCN, thereby reducing the overall yield of (Et₄N)₂(Fe₂OCl₆).

The red-brown crystalline needles of (Et₄N)₂(Fe₂OCl₆) lose solvent from the lattice on standing in the air, yielding a golden-brown powder, but show no signs of further decomposition. Th IR spectrum (Nujol mull) exhibits a νₕ₋ₒ–Fe band at 855 cm⁻¹. The UV–vis spectrum (MeCN) shows absorption maxima at 244, 292, 319(sh), and 376(sh) nm. Solutions of (Et₄N)₂(FeOCl₆) in MeCN decompose on standing for several hours at room temperature.²
Acknowledgment

We would like to thank the University of Cambridge, the EPSRC, and the
Newton Trust for financial support (JIL) KRD acknowledges the Centre for Funda-
mental Materials Research at Michigan State University for SQUID suscept-
ibility measurements and NSF for partial funding of this research.

References

(b) P. N. Turnowski, W. H. Turnowski, W. H. Armstrong, S. Liu, S. N. Brown, and S. J. Lippard,
cited therein.
9. (a) J.-S. Sun, Ph.D. dissertation, Michigan State University, 1994; (b) manuscript in preparation.

15. TETRAETHYLAMMONIUM-TETRATHIOPERRHENATE
Et₄N(ReS₄)

Submitted by JONATHAN T. GOODMAN and THOMAS B. RACHTFUSS
Checked by MADELI CASTRUITA, RAQUEL TERROBA,
and JONATHAN M. McCONNACHIE†

Known since the work of Berzelius, the tetrathiometallates, anions of the formula
MS₄²⁻, represent one of the fundamentally important classes of soluble metal
sulfides.¹ Of these anions, ReS₄ is unique in displaying high reactivity toward
unsaturated organic compounds.²⁻⁵ ReS₄⁻ has also been shown to form com-
plexes with a variety of metal ions.⁶ Tetrathioperrhenate is reduced at −1.58 V

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†Exxon Research and Engineering Co., Annandale, NJ 0880.