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13. TRANSITION METAL *p*-TOLUENESULFONATES

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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 hexafluorophosphate, tetrafluoroborate, tetraarylborate, and trifluoromethanesulfonate (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,[1] whereas tetraarylborate anions (including fluorinated analogs) have relatively reactive B-C bonds, and the aryl rings can coordinate in a pi fashion to metal centers.[2–4] The triflates[5,6] are moderately expensive to prepare and occasionally difficult to crystallize.

Binary transition metal *p*-toluenesulfonates (tosylates) 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},[8] Cr^{II},[9] Cr^{III},[10,11] Mn^{II},[11,12] $Fe^{II,III}$,[11,13] Co^{II},[11,14-16] Ni^{II},[11,14-17] Cu^{II},[11,15-18] and $Ru^{II,III}$,[19] as well as for Sc^{III},[20] Y^{III},[20] and the lanthanides Sm^{III}, Gd^{III}, Dy^{III}, Ho^{III}, Er^{III}, and Yb^{III}.[20] Alkali metal tosylates have also been briefly described for Li, Na, K, and Cs.[21] 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 for the anhydrous tosylate salts are presented in Table I. The IR spectra of the hydrated salts (Table II) are essentially identical to those of the anhydrous salts (Table III), 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]

Compound	ν(OH)	ν(CH)	Overtone	δ(CH)	$\nu_a(SO_2)$	$\nu_s(SO_2)$	δ(CH)	δ(CH)	δ(CH)	ν(SO)	δ(CS)?
	(vs, br)	(w)	(w)	(s)	(vs)	(vs)	(vs)	(vs)	(vs)	(vs)	(vs)
$[Ti(OH_2)_4][OTs]_3$	3329	3067 3050	1924	1653	1254 1153	1109	1033	1009	818	684	567
$[V(OH_2)_6][OTs]_3$	3399 3289	3040 3028	1914	1676 1650	1190	1127	1040	1013	814	682	566
$[VO(OH_2)_5][OTs]_2$	3425 3188		1918	1697 1654	1196	1127	1038	1011	811	685	569
$[Cr(OH_2)_4][OTs]_2$	3884 3355	3064 3032	1912	1666 1649	1234 1205 1183	1124	1040	1014	812	682	567
$[Cr(OH_2)_6][OTs]_3$	3155		1927	1662	1211 1155	1127	1037	1014	823	687	563
$[Mn(OH_2)_4]$ $[OTs]_2 \cdot H_2O$	3426 3268	3040 3028	1915	1669 1644	1192	1128	1041	1013	814	684	568
$[Fe(OH_2)_6][OTs]_2$	3396	3066 3041 3027	1914	1669 1646	1192	1128	1041	1013	814	684	569
$[Co(OH_2)_6][OTs]_2$	3408	3066 3028	1914	1670 1646	1189	1128	1040	1013	814	684	568
$[Ni(OH_2)_6][OTs]_2$	3407		1915	1669 1650	1191	1128	1040	1013	814	683	566

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

a published method.[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 *p*-toluenesulfonic acid hydrate (Acros, Aldrich) were used as received. Anhydrous *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.

■ **Caution.** *Solid p-toluenesulfonic acid and its solutions are corrosive.*

A. TETRAQUOTITANIUM(III)TRIS-*p*-TOLUENESULFONATE

$$Ti + 3\ HOTs \cdot H_2O + H_2O \rightarrow [Ti(OH_2)_4](OTs)_3 + {}^3/_2\ H_2$$

To –325-mesh titanium powder (1.19 g, 24.8 mmol) in a 250-mL, round-bottomed flask equipped with a reflux condenser is added *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 $C_{21}H_{29}O_{13}S_3Ti$: C, 39.8; H, 4.62; S, 15.2. Found: C, 39.5; H, 5.13; S, 15.8.

Properties

Pale purple $[Ti(OH_2)_4](OTs)_3$ 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

$$TiCl_3 + 3\ HOTs \rightarrow Ti(OTs)_3 + 3\ HCl$$

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_2O (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_2O (5 mL), and cooling to -20˚C. Yield: 4.12 g (67.1%).

Anal. Calcd. for $C_{21}H_{21}O_9S_3Ti$: 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. HEXAQUOVANADIUM(III)TRIS-*p*-TOLUENESULFONATE

$$V + 3\ HOTs{\cdot}H_2O + 3\ H_2O \rightarrow [V(OH_2)_6](OTs)_3 + 3/2\ H_2$$

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 $C_{21}H_{33}O_{15}S_3V$: 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

$$VCl_3 + 3\ HOTs \rightarrow V(OTs)_3 + 3\ HCl$$

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 Et_2O (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 is 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 is extracted with a refluxing mixture of 10:1 acetonitrile and methanol (10 mL). Cooling the hot extract to room temperature afforded additional green material, which is dried as described above. Yield: 7.20 g (91.6%).

Anal. Calcd. for $C_{21}H_{21}O_9S_3V$: 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 $[V(OH_2)_6][OTs]_3$ at 160˚C under vacuum (see below).

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

$$VO(acac)_2 + 2\ HOTs{\cdot}H_2O + {}^7/_2\ H_2O \rightarrow [VO(OH_2)_5](OTs)_2{\cdot}0.5H_2O + 2\ Hacac$$

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 H_2O (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 mixture 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 Et_2O (20 mL), and dried overnight under vacuum at room temperature. Yield: 8.97 g (94.7%).

Anal. Calcd. for $C_{14}H_{25}O_{12.5}S_2V$: 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 $[VO(OH_2)_5](OTs)_2 \cdot 0.5H_2O$ can be stored indefinitely at room temperature. It is soluble in methanol and water, but is insoluble in acetonitrile.

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

$$Cr + 2\,HOTs \cdot H_2O + 2\,H_2O \rightarrow [Cr(OH_2)_4](OTs)_2 + H_2$$

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 $C_{14}H_{22}O_{10}S_2Cr$: 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 $[Cr(OH_2)_4](OTs)_2$ 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

$$Cr + 3\,HOTs \cdot H_2O + {}^1/_4\,O_2 + {}^5/_2\,H_2O \rightarrow [Cr(OH_2)_6](OTs)_3 + H_2$$

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*-toluenesulfonic 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 diethylether (60 mL), and dried under vacuum overnight at 25°C. Yield: 11.5 g (88.5%).

Anal. Calcd. for $C_{21}H_{33}O_{15}S_3Cr$: 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 $[Cr(OH_2)_6](OTs)_3$ 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

$$Mn + 2\ HOTs{\cdot}H_2O + 3\ H_2O \rightarrow [Mn(OH_2)_4](OTs)_2{\cdot}H_2O + H_2$$

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 $C_{14}H_{24}O_{11}S_2Mn$: 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 $[Mn(OH_2)_4](OTs)_2{\cdot}H_2O$ 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

$$Fe + 2\ HOTs{\cdot}H_2O + 4\ H_2O \rightarrow [Fe(OH_2)_6](OTs)_2 + H_2$$

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 formed within 2 h. The crystals are collected by filtration and dried overnight under vacuum at room temperature. A second crop of crystals can be obtained by concentrating the mother liquor. Yield: 15.85 g (88.5%).

Anal. Calcd. for $C_{14}H_{26}O_{12}S_2Fe$: C, 33.2; H, 5.19; Fe, 11.0. Found: C, 33.7; H, 5.16; Fe, 11.5.

Properties

Pale green $[Fe(OH_2)_6](OTs)_2$ can be stored indefinitely at room temperature under an inert atmosphere. It is soluble in methanol and water, but is insoluble in acetonitrile and diethylether.

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

$$FeCl_3 + 3\ HOTs{\cdot}H_2O \rightarrow Fe(OTs)_3 + 3\ HCl + 3\ H_2O$$

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 diethylether (30 mL). The solid treated with methanol (30 mL) and the mixture is 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 is 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 diethylether (20 mL), and dried for 30 min under vacuum at 160˚C. Yield: 10.6 g (95.0%).

Anal. Calcd. for $C_{21}H_{21}O_9S_3Fe$: 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, diethylether, and hydrocarbons.

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

$$Co + 2\,HOTs{\cdot}H_2O + 4\,H_2O \rightarrow [Co(OH_2)_6](OTs)_2 + H_2$$

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 formed after 2 h. The crystals are collected by filtration and dried overnight under vacuum at room temperature. A second crop of crystals is obtained by concentration and cooling of the mother liquor. Yield: 16.75 g (53.8%).

Anal. Calcd. for $C_{14}H_{26}O_{12}S_2Co$: 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

$$Ni + 2\,HOTs{\cdot}H_2O + 4\,H_2O \rightarrow [Ni(OH_2)_6](OTs)_2 + H_2$$

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 remained. 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. A second crop of crystals is obtained by concentrating and cooling the mother liquor. Yield: 22.61 g (52.4%).

Anal. Calcd. for $C_{14}H_{26}O_{12}S_2Ni$: C, 33.0; H, 4.96; Ni, 11.5. Found: C, 33.2; H, 5.17; Ni, 11.5.

Properties

Pale green $[Ni(OH_2)_6](OTs)_2$ can be stored indefinitely at room temperature under an inert atmosphere. It is soluble in methanol and water, but is insoluble in acetonitrile and diethylether.

M. CESIUM-*p*-TOLUENESULFONATE

$$CsCl + HOTs{\cdot}H_2O \rightarrow CsOTs + HCl + H_2O$$

Solid CsCl (5.83 g, 34.6 mmol) and *p*-toluenesulfonic 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 diethylether (30 mL). Yield: 8.01 g (76.1%).

Anal. Calcd. for $C_7H_7O_3SCs$: 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 diethylether.

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[a]

Compound	ν(CH) (w)	Overtone (w)	$\nu_a(SO_2)$ (vs)	$\nu_s(SO_2)$ (vs)	δ(CH) (vs)	δ(CH) (vs)	δ(CH) (vs)	ν(SO) (vs)	δ(CS)? (vs)
$Ti(OTs)_3$	3094	1919	1298	1149	1040	1010	819	683	564
	3062	—	—	1120	—	—	—	—	—
$V(OTs)_3$	3060	1923	1291	1130	1073	1016	820	685	571
	3040	—	—	—	—	—	—	—	—
$VO(OTs)_2$	3066	1921	1282	1129	1063	1015	814	683	561
	3031	—	1267	—	—	—	—	—	—
$Cr(OTs)_2$	3060	1917	1235	1161	1060	1015	817	688	575
	3039	—	—	—	—	—	—	—	—
$Mn(OTs)_2$	3060	1920	1200	1144	1065	1017	815	690	574
	3037	—	—	—	—	—	—	—	—
$Fe(OTs)_2$	3061	1920	1195	1143	1065	1018	815	688	576
	3039	—	—	—	—	—	—	—	—
$Fe(OTs)_3$	3062	1920	1298	1125	1040	1010	814	687	562
	3039	—	1287	1116	—	—	—	—	—
$Co(OTs)_2$	3061	1920	1194	1142	1065	1018	819	686	576
	3039	—	—	—	—	—	—	—	—
$Ni(OTs)_2$	3063	1921	1201	1142	1067	1018	816	686	577
	3041	—	—	—	—	—	—	—	—
Cs(OTs)	3045	1940	1223	1128	1037	1015	823	682	564
		—	1195						

[a] Frequencies in cm^{-1}

Properties

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

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