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NEW TRANSITION METAL OXYTRIFLUOROMETHANESULFONATE SALTS

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SUMMARY

The reaction of $(CF_3SO_2)_2O$ with salts containing a transition metal in a high oxidation state results in the formation of new transition metal oxytrifluoromethanesulfonate salts.

INTRODUCTION

Salts containing the trifluoromethanesulfonate group (CF_3SO_3-) have been prepared via reaction of trifluoromethanesulfonic acid (CF_3SO_3H) with a variety of metal and nonmetal compounds [1-7]. The use of trifluoromethanesulfonic anhydride, [$(CF_3SO_2)_2O$], in preparing salts containing the CF_3SO_3- group, particularly salts containing a transition metal in a high oxidation state, has received limited study [8].

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RESULTS AND DISCUSSION

We have found that the following reactions, using $(CF_3SO_2)_2O$, produce new transition metal oxysalts containing the CF_3SO_3- group:

$$K_2CrO_4 + 2(CF_3SO_2)_2O \text{ —— } K_2CrO_2(CF_3SO_3)_4 \qquad (1)$$

$$K_2Cr_2O_7 + 3(CF_3SO_2)_2O \text{ —— } 2KCrO_2(CF_3SO_3)_3 \qquad (2)$$

$$PbCrO_4 + 2(CF_3SO_2)_2O \text{ —— } PbCrO_2(CF_3SO_3)_4 \qquad (3)$$

$$Na_2MoO_4 + 2(CF_3SO_2)_2O \text{ —— } Na_2MoO_2(CF_3SO_3)_4 \qquad (4)$$

$$Na_2WO_4 + 2(CF_3SO_2)_2O \text{ —— } Na_2WO_2(CF_3SO_3)_4 \qquad (5)$$

Also, it was found that a titanium salt containing CF_3SO_3- groups could be prepared by the following reaction:

$$K_2TiF_6 + 6(CF_3SO_2)_2O \text{ —— } K_2Ti(CF_3SO_3)_6 + 6CF_3SO_2F \qquad (6)$$

All of these salts are hygroscopic and are stable up to at least 90°C. The infrared spectra for all these compounds are listed in Table I. In general, based on published data for ionic and covalent bonded monodentate CF_3SO_3- groups [1,9,10] tentative assignments can be made for these compounds. For these new salts the absorption bands in the 1305-1347 cm^{-1} region and the 1231-1247 cm^{-1} region can be ascribed to the νasym SO_2 and νsym SO_2 stretching vibrations respectively. The νasym CF_3 and νsym CF_3 bands are probably located in the 1260-1265 cm^{-1} and 1171-1182 cm^{-1} regions, respectively. The M-O stretching vibrations are assigned to the 1031-1044 cm^{-1} region by comparison to $M_2YO_2(PO_2F_2)_4$ salts where M = Na^+, K^+ and Y = Cr,W,Mo[11]. Other probable assignments are: 766-770 cm^{-1}, C-S stretch; 640-643 cm^{-1}, δSO_2; 580-586 cm^{-1}, δsym CF_3; and 520-521 cm^{-1}, δasym CF_3. In general, these assignments favor a covalently bonded monodentate $-OSO_2CF_3$ group.

TABLE I

I.R. Spectra of Solid Trifluoromethanesulfonate Salts (cm^{-1})

$K_2CrO_2(CF_3SO_3)_4$	$PbCrO_2(CF_3SO_3)_4$	$KCrO_2(CF_3SO_3)_3$
1347(m)	1345(m)	1344(m)
1325(m)	1326(m)	1328(m)
1263(s,br)	1261(s)	1263(s)
1247(s)	1235(s,sh)	1231(m,sh)
1182(m)	1180(m)	1180(m)
1032(s)	1031(s)	1035(s)
1010(m)	1009(m,sh)	1011(m,sh)
955(m)	957(m)	952(s)
766(w)	905(w)	905(w)
640(m)	852(w,br)	885(w)
609(w,sh)	766(w)	795(m)
582(m)	640(s)	765(m)
520(m)	608(w,sh)	642(m,s)
	580(m)	582(w)
	520(m)	521(m)

$Na_2MoO_2(CF_3SO_3)_4$	$Na_2WO_2(CF_3SO_3)_4$	$K_2Ti(CF_3SO_3)_6$
1345(w,sh)	1345(w,sh)	1345(w,sh)
1305(w,sh)	1307(m,sh)	1262(s)
1260(s)	1265(s)	1232(s,sh)
1235(s,sh)	1232(s,sh)	1208(m,sh)
1173(s,br)	1171(s)	1180(s)
1034(s)	1044(s)	1032(s)
952(m)	1035(s,sh)	1028(s,sh)
919(m)	764(m)	861(m)
766(m)	643(s)	770(m)
642(s)	580(m)	650(s,sh)
580(m)	520(m)	640(s)
520(s)		586(m)
		520(m)

EXPERIMENTAL

$(CF_3SO_2)_2O$ was purchased from PCR Research Chemicals and was vacuum distilled prior to use. The infrared (IR) spectrum agreed with the published spectrum. The following salts were purchased from Mallinckrodt (AR) grade: $K_2Cr_2O_7$, K_2CrO_4, Na_2MoO_4 and Na_2WO_4. These salts and $PbCrO_4$ (Baker and Adamson reagent grade, 98%), and K_2TiF_6 (Alfa, 98%) were used as received after drying.

Infrared spectra were recorded with a Perkin-Elmer model 467 infrared spectrophotometer. Gas-phase spectra were obtained with a Monel cell using either AgCl or NaCl windows (path length of the cell was 8.25 cm). Solid-phase spectra were recorded between NaCl and KRS-5 windows (neat) or as KBr pellets. The spectra were calibrated with a polystyrene film. X-rays results were obtained using an XRD-5 General Electric powder camera. The samples were contained in 0.5 mm capillaries; only medium (m) to very strong (vs) intensities lines are reported. Standard analyses were performed by Beller Laboratories in Göttingen, West Germany.

General Procedure

The reaction vessels (Pyrex glass) used in the following synthetic runs with metal oxide salts had a volume of 100 ml and were equipped with a Kontes Teflon stopcock and a Teflon-covered stirring bar.

The metal oxide salt was transferred to a reaction vessel and then dried in vacuo. Excess $(CF_3SO_2)_2O$ was then added. The mixture was magnetically stirred and after it was essentially complete the volatile materials were removed by pumping through a trap cooled to -196°. The remaining solid was pumped until constant weight was achieved. For most reactions the constant weight was used to determine the composition of the solid product as no other products were formed.

Preparation of $K_2CrO_2(CF_3SO_3)_4$

To 1.46 mmol of K_2CrO_4, 23.6 mmol of $(CF_3SO_2)_2O$ was added. The mustard yellow product [1.57 mmol of $K_2CrO_2(CF_3SO_3)_4$] was formed at room temperature (2d) and 50-60° (9d). The compound dec. ∿ 93°. A powder spectrum gave the following d values (in Å) along with their respective intensities: 11.38(m), 9.99(m), 5.32(m), 4.88(m), 4.66(s), 3.90(vs).

Anal. Calcd for $K_2CrO_2(CF_3SO_3)_4$: Cr, 6.85; C, 6.33; S, 16.91; F, 30.06. Found: Cr, 6.82; C, 6.17; S, 16.95; F, 29.6.

Preparation of $KCrO_2(CF_3SO_3)_3$

To 0.753 mmol of $K_2Cr_2O_7$, 48.3 mmol of $(CF_3SO_2)_2O$ was added. The tan solid [1.51 mmol of $KCrO_2(CF_3SO_3)_3$] was formed at room temperature (38d) in essentially 100% yield. The product dec. at 160°. A powder spectrum gave the following d values (in Å) along with their respective intensities: 10.36(m), 9.01(ms), 7.86(m), 4.97(s), 4.73(vs), 4.29(s), 3.91(vs), 2.89(m), 2.34(ms).

Anal. Calcd for $KCrO_2(CF_3SO_3)_3$: Cr, 9.11; C, 6.32; S, 16.87; F, 30.0. Found: Cr, 8.88; C, 6.49; S, 16.78; F, 30.7.

Preparation of $PbCrO_2(CF_3SO_3)_4$

To 0.827 mmol of $PbCrO_4$, 10.7 mmol of $(CF_3SO_2)_2O$ was added. The tan-orange solid [0.821 mmol of $PbCrO_2(CF_3SO_3)_4$] was formed at room temperature (9d) and 40-50° (8d) in essentially

100% yield. The product decomposes ∿90°. A powder spectrum gave the following d values (in Å) along with their respective intensities: 12.55(m), 10.13(s), 3.92(m), 3.03(m), 2.92(m), 2.62(m), 2.55(m), 2.47(m).

Anal. Calcd for $PbCrO_2(CF_3SO_3)_4$: Cr, 5,86; C, 5.41; S, 14.45; F, 25.7. Found: Cr, 5.67; C, 6.05; S, 12.09; F, 21.1.

Preparation of $Na_2MoO_2(CF_3SO_3)_4$

To 1.18 mmol of Na_2MoO_4, 13.7 mmol of $(CF_3SO_2)_2O$ was added. The white solid (slight blue tinge), 1.12 mmol of $Na_2MoO_2(CF_3SO_3)_4$ was formed at r.t. (2d) and 60° (6d) in 95% yield. The product decomposes ∿160°. A powder spectrum gave the following d values (in Å) along with their respective intensities: 12.13(m), 6.76(s), 6.01(vs), 4.97(m), 4.76(s), 4.61(s), 4.10(s), 3.72(s), 3.27(m), 2.84(m).

Anal. Calcd for $Na_2MoO_2(CF_3SO_3)_4$: C, 6.24; S, 16.65; F, 29.6. Found: C, 6.09; S, 15.92; F, 28.4.

Preparation of $Na_2WO_2(CF_3SO_3)_4$

To 0.947 mmol of Na_2WO_4, 20.9 mmol of $(CF_3SO_2)_2O$ was added. The white solid [0.906 mmol of $Na_2WO_2(CF_3SO_3)_4$] was formed at r.t. (2d) and 60-70° (11d) in 96% yield. The product melted at 242±2°. A powder spectrum gave the following d values (in Å) along with their respective intensities: 11.18(m), 10.66(s), 7.66(m), 4.91(s), 4.74(s), 4.03(m), 3.81(s), 3.31(m), 3.23(m), 2.91(s), 2.81(m).

Anal. Calcd for $Na_2WO_2(CF_3SO_3)_4$: C, 5.60; S, 14.95; F, 26.57. Found: C, 5.25; S, 13.76; F, 25.0.

Preparation of $K_2Ti(CF_3SO_3)_6$

To 0.547 mmol of K_2TiF_6, 15.3 mmol of $(CF_3SO_2)_2O$ was added. The white solid [0.547 mmol of $K_2Ti(CF_3SO_3)_6$] was formed in the dark at r.t. (29 d) in 100% yield. The product melted above 110° to a clear liquid. The volatile product CF_3SO_2F, was identified by its characteristic infrared spectrum. The powder spectrum gave the following d values (in Å) along with their respective intensities: 8.70(ms), 4.85(m), 4.54(ms) 4.38(ms), 3.95(s), 3.66(m), 3.30(m), 2.71(m), 2.55(m), 2.34(m).

Anal. Calcd for $K_2Ti(CF_3SO_3)_6$: C, 7.06; S, 18.85; F, 33.5. Found: C, 6.12; S, 16.75; F, 31.8.

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