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NEW TRANSITION METAL OXYTRIFLUOROMETHANESULFONATE SALTS

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SUMMARY

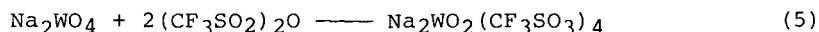
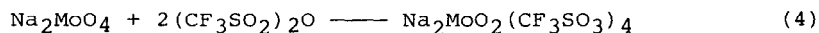
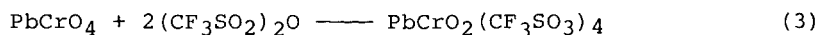
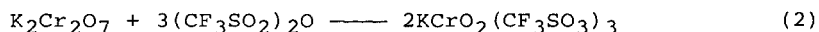
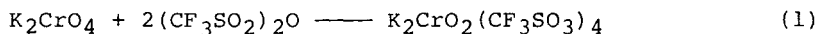
The reaction of  $(\text{CF}_3\text{SO}_2)_2\text{O}$  with salts containing a transition metal in a high oxidation state results in the formation of new transition metal oxytrifluoromethanesulfonate salts.

INTRODUCTION

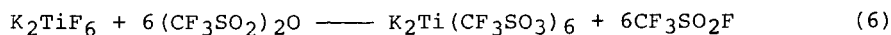
Salts containing the trifluoromethanesulfonate group ( $\text{CF}_3\text{SO}_3^-$ ) have been prepared via reaction of trifluoromethanesulfonic acid ( $\text{CF}_3\text{SO}_3\text{H}$ ) with a variety of metal and nonmetal compounds [1-7]. The use of trifluoromethanesulfonic anhydride,  $[(\text{CF}_3\text{SO}_2)_2\text{O}]$ , in preparing salts containing the  $\text{CF}_3\text{SO}_3^-$  group, particularly salts containing a transition metal in a high oxidation state, has received limited study [8].

## RESULTS AND DISCUSSION

We have found that the following reactions, using  $(\text{CF}_3\text{SO}_2)_2\text{O}$ , produce new transition metal oxysalts containing the  $\text{CF}_3\text{SO}_3^-$  group:



Also, it was found that a titanium salt containing  $\text{CF}_3\text{SO}_3^-$  groups could be prepared by the following reaction:



All of these salts are hygroscopic and are stable up to at least  $90^\circ\text{C}$ . The infrared spectra for all these compounds are listed in Table I. In general, based on published data for ionic and covalent bonded monodentate  $\text{CF}_3\text{SO}_3^-$  groups [1,9,10] tentative assignments can be made for these compounds. For these new salts the absorption bands in the  $1305\text{-}1347\text{ cm}^{-1}$  region and the  $1231\text{-}1247\text{ cm}^{-1}$  region can be ascribed to the  $\nu_{\text{asym}}\text{SO}_2$  and  $\nu_{\text{sym}}\text{SO}_2$  stretching vibrations respectively. The  $\nu_{\text{asym}}\text{CF}_3$  and  $\nu_{\text{sym}}\text{CF}_3$  bands are probably located in the  $1260\text{-}1265\text{ cm}^{-1}$  and  $1171\text{-}1182\text{ cm}^{-1}$  regions, respectively. The M-O stretching vibrations are assigned to the  $1031\text{-}1044\text{ cm}^{-1}$  region by comparison to  $\text{M}_2\text{YO}_2(\text{PO}_2\text{F}_2)_4$  salts where  $\text{M} = \text{Na}^+, \text{K}^+$  and  $\text{Y} = \text{Cr}, \text{W}, \text{Mo}$  [11]. Other probable assignments are:  $766\text{-}770\text{ cm}^{-1}$ , C-S stretch;  $640\text{-}643\text{ cm}^{-1}$ ,  $\delta\text{SO}_2$ ;  $580\text{-}586\text{ cm}^{-1}$ ,  $\delta_{\text{sym}}\text{CF}_3$ ; and  $520\text{-}521\text{ cm}^{-1}$ ,  $\delta_{\text{asym}}\text{CF}_3$ . In general, these assignments favor a covalently bonded monodentate  $-\text{OSO}_2\text{CF}_3$  group.

TABLE I

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

$\text{K}_2\text{CrO}_2(\text{CF}_3\text{SO}_3)_4$	$\text{PbCrO}_2(\text{CF}_3\text{SO}_3)_4$	$\text{KCrO}_2(\text{CF}_3\text{SO}_3)_3$
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)
$\text{Na}_2\text{MoO}_2(\text{CF}_3\text{SO}_3)_4$	$\text{Na}_2\text{WO}_2(\text{CF}_3\text{SO}_3)_4$	$\text{K}_2\text{Ti}(\text{CF}_3\text{SO}_3)_6$
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

$(\text{CF}_3\text{SO}_2)_2\text{O}$  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:  $\text{K}_2\text{Cr}_2\text{O}_7$ ,  $\text{K}_2\text{CrO}_4$ ,  $\text{Na}_2\text{MOO}_4$  and  $\text{Na}_2\text{WO}_4$ . These salts and  $\text{PbCrO}_4$  (Baker and Adamson reagent grade, 98%), and  $\text{K}_2\text{TiF}_6$  (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  $\text{AgCl}$  or  $\text{NaCl}$  windows (path length of the cell was 8.25 cm). Solid-phase spectra were recorded between  $\text{NaCl}$  and  $\text{KRS-5}$  windows (neat) or as  $\text{KBr}$  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  $(\text{CF}_3\text{SO}_2)_2\text{O}$  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  $-196^\circ$ . 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.  $\sim 93^\circ$ . 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  $\sim 90^\circ$ . A powder spectrum gave the following  $d$  values (in  $\text{\AA}$ ) 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  $\text{PbCrO}_2(\text{CF}_3\text{SO}_3)_4$ : 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 $\text{Na}_2\text{MoO}_2(\text{CF}_3\text{SO}_3)_4$

To 1.18 mmol of  $\text{Na}_2\text{MoO}_4$ , 13.7 mmol of  $(\text{CF}_3\text{SO}_2)_2\text{O}$  was added. The white solid (slight blue tinge), 1.12 mmol of  $\text{Na}_2\text{MoO}_2(\text{CF}_3\text{SO}_3)_4$  was formed at r.t. (2d) and  $60^\circ$  (6d) in 95% yield. The product decomposes  $\sim 160^\circ$ . A powder spectrum gave the following  $d$  values (in  $\text{\AA}$ ) 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  $\text{Na}_2\text{MoO}_2(\text{CF}_3\text{SO}_3)_4$ : C, 6.24; S, 16.65; F, 29.6. Found: C, 6.09; S, 15.92; F, 28.4.

#### Preparation of $\text{Na}_2\text{WO}_2(\text{CF}_3\text{SO}_3)_4$

To 0.947 mmol of  $\text{Na}_2\text{WO}_4$ , 20.9 mmol of  $(\text{CF}_3\text{SO}_2)_2\text{O}$  was added. The white solid [0.906 mmol of  $\text{Na}_2\text{WO}_2(\text{CF}_3\text{SO}_3)_4$ ] was formed at r.t. (2d) and  $60-70^\circ$  (11d) in 96% yield. The product melted at  $242 \pm 2^\circ$ . A powder spectrum gave the following  $d$  values (in  $\text{\AA}$ ) 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  $\text{Na}_2\text{WO}_2(\text{CF}_3\text{SO}_3)_4$ : 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  $110^\circ$  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  $\text{\AA}$ ) 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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### REFERENCES

- 1 J.R. Dalziel and F. Aubke, *Inorg. Chem.*, 12, 2707 (1973).
- 2 R.E. Nofhle and G.H. Cady, *Inorg. Chem.*, 5, 2182 (1966).
- 3 S.K. Yarboro, R.E. Nofhle, and W.B. Fox, *J. Fluorine Chem.*, 6, 187 (1975).
- 4 M.B. Dines, *Sep. Sci.*, 8, 661 (1973).
- 5 C.L. Jenkins and J.K. Kochi, *J. Am. Chem. Soc.*, 94, 843 (1972).
- 6 K.F. Thom, U.S. Patent 3,615,169 (1971); U.S. Patent 3,725,296 (1973) and U.S. Patent 3,796,738 (1974).
- 7 J. Massaux and G. Duyckaerts, *Anal. Chem. Acta*, 73, 416 (1974).
- 8 M.B. Dines, *J. Organomet. Chem.*, 67, C55 (1974).
- 9 M.G. Miles, G. Doyle, R.P. Cooney, and R.S. Tobias, *Spectrochimica Acta*, 25, 1515 (1969).

- 10 H. Bürger, K. Burczyk, and A. Blaschette, *Montash. Chem.*, 101, 102 (1970).
- 11 S.D. Brown, L.M. Emme, and G.L. Gard, *J. Inorg. Nucl. Chem.*, 3 2557 (1975).