TABLE II

INTERATOMIC DISTANCES AND ANGLES

Distance	Value, Å	Angle	Value, deg
Re–O	1.781 (3)–1.87[a]	Cl–Re–C2	87.9 (1)
Re–Cl	2.139 (3)–1.91[a]	Cl–Re–O	91.5 (1)
Re–C2	2.130 (3)–1.91[a]	C2–Re–O	90.1 (1)
Cl–N1	1.156 (5)–1.15[a]	Re–Cl–N1	173.4 (3)
C2–N2	1.154 (5)	Re–C2–N2	178.1 (5)
K1–N1	2.880 (4)	N2–K1–O	82.7 (3)
K1–N2	2.837 (4)	N1–K1–N2	85.2 (3)
K1–O	2.842 (3)	N1–K1–O	76.4 (3)
K2–O	2.843 (3)	O–K2–N1	122.9 (3)
K2–N1	2.803 (4)	O–K2–O	83.1 (3)
K2–N1	3.177 (4)	O–K2–N2	126.3 (3)
K2–N2	2.830 (4)	O–K2–N1	72.4 (3)
K2–N2	3.206 (4)	O–K2–N2	76.4 (3)
K2–O	2.796 (3)	N1–K2–N2	101.0 (3)
		O–K2–N1	138.5 (3)
		N1–K2–N1	83.2 (3)
		N1–K2–N2	84.7 (3)
		N2–K2–O	82.8 (3)
		N2–K2–N1	148.7 (3)
		N2–K2–N2	78.9 (3)
		O–K2–N1	74.4 (3)
		O–K2–N2	135.9 (3)
		N1–K2–N2	132.4 (3)

[a] Values reported in ref 2.

atom was confirmed by refinement of the isocyanide configuration. The resulting agreement factors, $R = 0.057$ and $r = 0.069$, were significantly poorer than with the cyanide arrangement and the thermal parameters were less reasonable in that the atoms attached to the rhenium displayed greater thermal motion than the external atoms.

The thermal ellipsoids are illustrated in Figures 1 and 2. The rhenium atom is nearly isotropic. Its maximum vibration nearly bisects the Cl–Re–O angle. For the carbon, nitrogen, and oxygen atoms the maximum vibration is essentially perpendicular to the bonds with the minimum directed along the bonds.

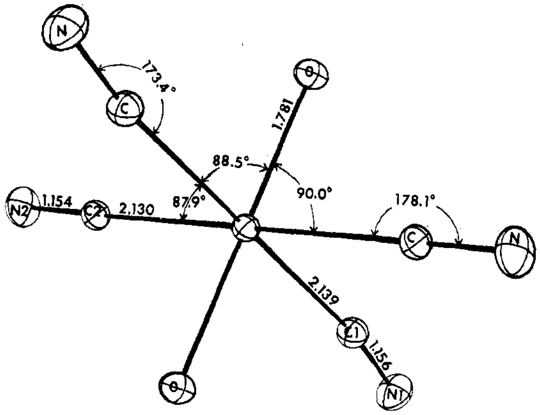

Figure 2.—Bond angles and distances in the ion $ReO_2(CN)_4^{3-}$.

Bond Distances and Angles.—The average potassium to oxygen distance (2.83 Å) and potassium to nitrogen distance (2.96 Å) are typical[10] ionic contacts. The C–N distances (1.155 (5) Å) are also quite typical. The deviation from 180° for the Re–C–N angles is due either to packing considerations or to interactions with the potassium ions. The 4.7° difference in these angles may come about through the nonequivalent interaction with potassium ions (Figure 1). Similar deviations from 180° Re–C–N angles have been observed[11] in $[Pt(NH_3)_4]_2[Re_2O_3(CN)_8]$. The Re–O distance (1.781 (3) Å) here reported is probably the best value known for a rhenium–oxygen "double bond" and is significantly longer than the multiple Re–O bond observed[12] in $[(C_2H_5)_4N][ReBr_4O(OH_2)]$ of 1.71 (4) Å.

Conclusion

The crystal structure of $K_3ReO_2(CN)_4$ has been redetermined and shows significant differences from the earlier study. The basic structure of the negative ion was confirmed and the accuracy and precision of the bond angles and distances were significantly improved. In a subsequent communication comparison of these anion parameters with those of $ORe(CN)_4ORe(CN)_4O^{4-}$ will be made.[11]

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Reactions of Peroxydisulfuryl Difluoride To Give Oxyfluorosulfates of Metals in High Oxidation State

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There are a number of routes by which inorganic fluorosulfates have been prepared.[1–6]

Peroxydisulfuryl difluoride has been shown to be an efficient sulfonating and oxidizing agent.[6] Until recently a very few fluorosulfates of transition metals were known, particularly in their higher oxidation states. This paper reports the syntheses of oxyfluorosulfates of several transition metals in their higher oxidation states.

Experimental Section

Materials.—Peroxydisulfuryl difluoride was prepared by the reaction of fluorine with sulfur trioxide[7] and purified by prolonged pumping of the crude product held at −78°. Ir analysis and vapor density measurements indicated that the product was substantially pure.

The carbonates of manganese, cobalt, nickel, silver, and thallium of Baker Analyzed reagent grade were dried in an oven at 110° for 2 hr before use. Silver oxide was obtained by heating silver carbonate.

Preparation of Oxyfluorosulfates.—In a typical preparation, a known weight of the carbonate or oxide of the metal was treated in a closed glass vessel with an excess of peroxydisulfuryl difluoride. The latter was condensed into the reactor at −183° and the vessel was then allowed to warm to room temperature and stand for 3–12 hr. After the reaction appeared to be complete, the vessel was held at −40° while the volatile products were pumped away. These were later separated by fractional codistillation.[8] The nonvolatile products were dried under vacuum to constant weight. The weights of oxyfluorosulfates obtained from the respective metal carbonate or oxide are given in Table I.

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[2] W. Traube, *ibid.*, **46**, 2513 (1913).

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[6] J. M. Shreeve and G. H. Cady, *J. Amer. Chem. Soc.*, **83**, 4521 (1961).

[7] F. B. Dudley and G. H. Cady, *ibid.*, **79**, 513 (1957).

TABLE I
WEIGHTS, COLORS, AND ANALYSES OF METAL OXYFLUOROSULFATES

Compd	Wt, g	Wt of oxyfluorosulfate, g Calcd	Wt of oxyfluorosulfate, g Found	Oxyfluorosulfate	Color		Oxyfluorosulfate anal., % Calcd	Oxyfluorosulfate anal., % Found
$MnCO_3$	0.4680	0.6918	0.6952	$MnOSO_3F$	Brownish black	Mn	32.35	32.05
						S	18.82	18.68
						F	10.83	10.18
$CoCO_3$	0.4480	0.6549	0.6480	$CoOSO_3F$	Chocolate	Co	33.90	33.10
						S	18.39	18.00
						F	10.92	10.62
$NiCO_3$	0.4268	0.6245	0.6292	$NiOSO_3F$	Grayish black	Ni	33.79	33.00
						S	18.42	18.10
						F	10.96	10.64
Ag_2CO_3	0.6284	0.9790	0.9892	$Ag_2O(SO_3F)_2$	Black	Ag	50.23	49.80
Ag_2O	0.5264	0.9756	0.9740	$Ag_2O(SO_3F)_2$	Black	S	14.88	14.52
						F	8.86	8.24
Tl_2CO_3	0.5679	0.7740	0.7654	$TlOSO_3F$	Brown	Tl	63.99	62.54
						S	10.00	9.49
						F	5.95	5.35

Chemical Analysis.—Metals in the compounds were determined using standard methods.[9] Sulfur was determined as barium sulfate, while fluorine was determined using a fluoride ion sensitive electrode while titrating with thorium nitrate solution. Analytical results are given in Table I.

Discussion

The volatile products were found to be CO_2, $S_2O_5F_2$, O_2, unreacted $S_2O_6F_2$, and a trace of SiF_4. Probably the oxygen and pyrosulfuryl fluoride were formed by decomposition of part of the peroxydisulfuryl difluoride. The formation of oxyfluorosulfate from the carbonate of Mn, Co, or Ni can be represented by the general equation: $2MCO_3 + S_2O_6F_2 \rightarrow 2MO(SO_3F) + 2CO_2$ (M = Mn, Co, or Ni).

The oxyfluorosulfates of manganese, cobalt, nickel, and silver react with potassium iodide solution (made acidic with sulfuric acid) liberating both oxygen and iodine. To determine the number of oxidizing equivalents present per mole of the oxyfluorosulfate, it was necessary to measure both oxygen and iodine produced. To do this, a known weight of the salt was allowed to react with gas-free acidic solution of potassium iodide in a closed reactor. The vessel was then chilled to −183° and oxygen was pumped away. The loss in weight was that of the oxygen produced by the reaction. The amount of iodine was then determined by titration with standard sodium thiosulfate solution. Table II gives the results of these determinations and shows that each metal was reduced in oxidation state by one unit by reaction with acidic potassium iodide solution. Since the reduction would give Mn(II), Co(II), Ni(II), and Ag(I), it follows that oxyfluorosulfates contained Mn(III), Co(III), Ni(III), and Ag(II).

TABLE II
REACTIONS OF OXYFLUOROSULFATES WITH ACIDIC SOLUTION OF POTASSIUM IODIDE

Compd	Mol of salt $\times 10^3$	Mol of O_2 produced $\times 10^4$	Equiv of I_2 produced $\times 10^4$	Total equiv of $O_2 + I_2$ per mol of the salt
$MnOSO_3F$	5.98	14.18	5.75	1.04
$CoOSO_3F$	3.76	8.56	5.06	1.04
$NiOSO_3F$	4.39	10.81	5.01	1.09
$Ag_2O(SO_3F)_2$	0.83	3.75	1.70	2.01

Infrared spectra of the compounds were taken in the form of Nujol mulls between silver chloride disks. The instrument was a Beckmann IR 10 spectrometer. Since the compounds are good oxidizing agents, some of them may have reacted with Nujol. The spectra of $CoOSO_3F$ and $NiOSO_3F$ appeared to be of good quality. Peaks remaining after subtracting those for Nujol are listed in Table III. Spectra for salts of Mn, Ag, and Tl contained bands for S—F and S═O stretching in regions characteristic of fluorosulfates. Because of their rather poor quality in general, these spectra are not given.

TABLE III
INFRARED SPECTRA OF OXYFLUOROSULFATES[a]

$CoOSO_3F$	$NiOSO_3F$	Assignment	$CoOSO_3F$	$NiOSO_3F$	Assignment
1246 vs	1246 vs	S–O asym str	607 s	615 s	S–O asym def
1081 vs	1088 vs	S–O sym str	560 s	560 s	S–O sym def
832 vs	820 vs	S–F str	504 s	505 s	

[a] Key: vs, very strong; s, strong.

The S—F band in fluorosulfates of copper and iron has been reported around 840 cm^{-1} and the salts are believed to be covalent in nature.[10] The S—F band in these oxyfluorosulfates is around 840 cm^{-1} which is more characteristic of covalently bonded fluorosulfates rather than ionic fluorosulfates like potassium fluorosulfate, the S—F frequency for which is 750[10] or 732 cm^{-1}.[11]

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The Low-Temperature Magnetic Susceptibility of Tetra-μ_3-methoxy-tetrakis[salicylaldehydato-(ethanol)nickel(II)], a Complex with a Positive Exchange Coupling Constant

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The existence of multimetallic molecules which exhibit intramolecular magnetic exchange has been well known for many years, but until recently all docu-