

measurement of longitudinal axis or transition moment vector becomes possible.⁵

One important application emerging from our linear dichroism measurements is the possibility of distinguishing between *cis* and *trans* ring fusion in polycyclic ketones. This may be exemplified in 17 β -acetoxy-5 β - Δ^2 -androst-1-one in which the angle between its transition moment and the longitudinal axis of the molecule exceeds 50°. The d_0 found for this compound was <1 (0.8), in accord with our expectations.

(5) Since the direction of the transition moment is obtained from an absorption phenomenon measurement, which depends on a squared value, it is only possible to define the axis along which it is directed and not the absolute direction.

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Perbromyl Fluoride

Sir:

We have synthesized perbromyl fluoride, BrO₃F, by the reaction of potassium perbromate with antimony pentafluoride in anhydrous hydrogen fluoride. It is a highly volatile compound, with a vapor pressure of *ca.* 6 Torr at -80°. At room temperature the compound persists for many weeks in Kel-F or fluorinated metal apparatus, but with evidence of some decomposition or reaction.

The preparation of BrO₃F was suggested by the recent synthesis of stable perbromates^{1,2} and by the unusual stability of ClO₃F. The latter has been prepared by direct fluorination of potassium chlorate,³ and by reaction of potassium perchlorate with HSO₃F,⁴ with SbF₅,⁵ and with mixtures of the two.⁶ More recently it has been made by the reaction of potassium perchlorate with AsF₅ or SbF₅ dissolved in anhydrous HF, BrF₅, or IF₅.⁷ Periodyl fluoride, IO₃F, has been reported to result from the passage of fluorine through a solution of periodic acid in HF.⁸

Our experiments leading to the production of perbromyl fluoride were monitored with a time-of-flight mass spectrometer and associated metal vacuum system.⁹ Sodium bromate was found to react with elemental fluorine below room temperature to yield Br₂, Br₂O, BrO₂F, BrF₅, and O₂, but not detectable amounts of BrO₃F. Reaction of potassium perbromate with HSO₃F also failed to give BrO₃F, yielding instead Br₂ and O₂.

Perbromyl fluoride was successfully synthesized by a technique analogous to that used by Wamser, *et al.* to prepare ClO₃F.⁷ In a typical experiment, 0.2889 g (1.579 mmoles) of KBrO₄² was placed in a Kel-F

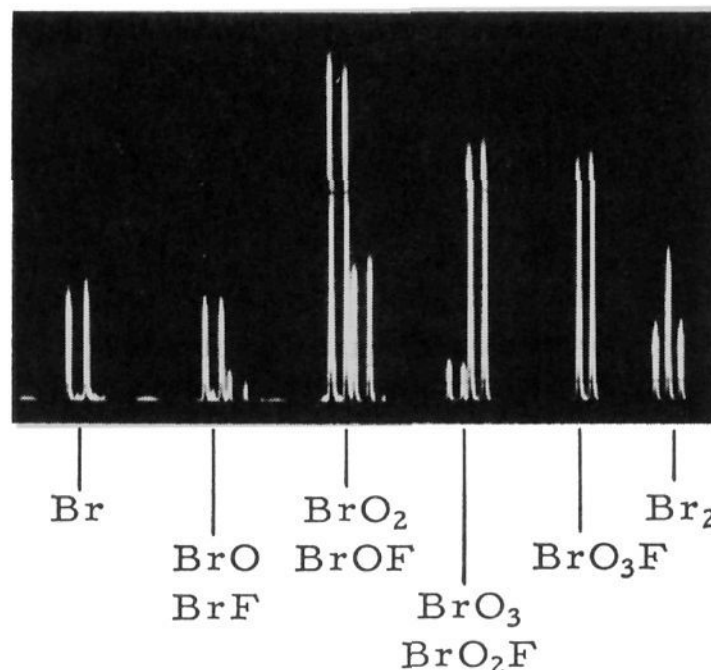


Figure 1. Mass spectrum of perbromyl fluoride.

tube. The tube was evacuated on a Monel vacuum line and chilled with liquid nitrogen; *ca.* 5 g of HF and 1.2 g of SbF₅ were vacuum distilled into it. The mixture was warmed to room temperature, agitated to dissolve the perbromate, and allowed to stand for 1 hr. The HF and SbF₅ were then removed by absorption on sodium fluoride, leaving 0.0380 \pm 0.0005 atm l. of gaseous product at 25°. The product contained no significant quantity of gas that could not be condensed in a liquid nitrogen bath. The condensed product weighed 0.2255 \pm 0.001 g, corresponding to a 97% yield of BrO₃F with an apparent molecular weight of 145 \pm 2 (calcd 146.9).

Samples of perbromyl fluoride for mass spectrometry were sometimes obtained simply by fractionally distilling the BrO₃F from the original mixture at temperatures between -80 and -100°. Figure 1 shows the mass spectrum of perbromyl fluoride and its fragments. These are readily characterized by the two nearly equally abundant bromine isotopes. Some of the Br₂ may have come from decomposition of the BrO₃F, but more is believed to have arisen from reaction of the compound with incompletely fluorinated surfaces of the spectrometer and its associated vacuum system.

Pure BrO₃F is a colorless gas or liquid solidifying at about -110° to a white solid. However, the solid and liquid are frequently colored yellow by decomposition and/or reaction products. The compound appears to be more reactive than ClO₃F. It hydrolyzes in alkaline solution at room temperature to give fluoride and perbromate.



This reaction provides a convenient method of analyzing the compound. Hydrolysis of the 0.2255 \pm 0.001 g (1.535 \pm 0.007 mmoles) sample mentioned earlier yielded 1.531 \pm 0.005 mmoles of BrO₄⁻ and 1.52 \pm 0.02 mmoles of F⁻. The reaction consumed 3.11 \pm 0.01 mmoles of base. The resulting solution contained only 6.6 \pm 0.2 \times 10⁻³ mequiv of oxidizing power attributable to lower oxidation states of bromine.

Detailed studies of the properties of perbromyl fluoride are now in progress. Efforts to synthesize IO₃F from KIO₄ by the analogous method failed to give an identifiable product.

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The Ionic Dissociation of Some Compounds Containing Covalent Metal-Metal Bonds

Sir:

The covalent nature of bonds between transition metals and many main group metals has been firmly established by numerous structural, spectroscopic, and chemical studies. Recent X-ray crystallographic studies have confirmed the presence of covalent metal-to-metal bonds in $\text{Hg}[\text{Co}(\text{CO})_4]_2$,¹ $\text{Zn}[\text{Co}(\text{CO})_4]_2$,² $(\text{C}_6\text{H}_5)_3$ -

$\text{cm}^2 \text{mole}^{-1}$ indicated that essentially complete dissociation had occurred. The air-sensitive solution exhibited a single, strong infrared absorption in the carbonyl stretching region at $1920 \pm 2 \text{ cm}^{-1}$. In a recent study, Edgell, Yang, and Koizumi⁷ showed that in aqueous solutions of $\text{NaCo}(\text{CO})_4$ the tetracarbonylcobaltate(−I) anion was characterized by a single infrared carbonyl stretching absorption at 1919 cm^{-1} in agreement with that predicted for a regular tetrahedral structure.

The foregoing observations suggested that the heterolytic cleavage of metal-metal bonds might be more common than previously anticipated. Because of the limited water solubility of many compounds of interest, especially those containing organic substituents, a study was undertaken using carefully purified *N,N*-dimethylformamide (DMF) as the ionizing solvent. Infrared and conductance data for some representative compounds are shown in Table I. It is obvious that

Table I. Conductivity and Infrared Data in DMF

No.	Compound	Λ_M^a	Infrared absorptions, cm^{-1} b,c
1	$\text{Zn}[\text{Co}(\text{CO})_4]_2$	111	1892 vs
2	$\text{Cd}[\text{Co}(\text{CO})_4]_2$	99	2051 vw, 1961 m, 1891 vs
3	$\text{Hg}[\text{Co}(\text{CO})_4]_2$	0.17	2065 m, 1994 s
4	$(\text{C}_6\text{H}_5)_3\text{SnCo}(\text{CO})_4$	56	1893 vs
5	$\text{Zn}[\text{Mn}(\text{CO})_5]_2$	103	2015 w, 1950 vw (sh), 1900 vs, 1865 vs
6	$\text{Cd}[\text{Mn}(\text{CO})_5]_2$	2.0	2075 w, 2052 m, 1960 vs, 1940 s (sh), 1900 w (sh), 1865 w
7	$(\text{C}_6\text{H}_5)_3\text{SnMn}(\text{CO})_5$	0.63	2102 m, 2040 w (sh), 1997 s, 1900 vw, 1867 vw
8	$\text{Zn}[\text{Cr}(\text{CO})_3\text{C}_5\text{H}_5]_2^d$	91	1892 s, 1775 s
9	$\text{Zn}[\text{Mo}(\text{CO})_3\text{C}_5\text{H}_5]_2^d$	78	1957 vw, 1897 s, 1871 vw (sh), 1840 vw, 1779 vs
10	$\text{Zn}[\text{W}(\text{CO})_3\text{C}_5\text{H}_5]_2^d$	64	1957 m, 1892 s, 1866 m, 1828 m, 1774 vs
11	$(\text{C}_6\text{H}_5)_3\text{SnMo}(\text{CO})_3\text{C}_5\text{H}_5$	0.27	1998 s, 1925 m, 1899 s
12	$\text{Zn}[\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5]_2^d$	0.14	2016 vw, 1937 s, 1926 s, 1869 s
13	$(\text{C}_6\text{H}_5)_3\text{SnFe}(\text{CO})_2\text{C}_5\text{H}_5$	0.015	1990 m, 1939 m
14	$\text{C}_5\text{H}_5(\text{CO})_2\text{FeZnCo}(\text{CO})_4^d$	55	1948 m, 1892 vs

^a Molar conductivity values are $\text{ohm}^{-1} \text{cm}^2 \text{mole}^{-1}$. All measurements were made at 1000 cps on 0.010 *M* solutions under an argon atmosphere. ^b Infrared spectra of the solutions used for the conductance measurements were observed under argon in a 0.1-mm sealed cell employing CaF_2 windows; the estimated accuracy is $\pm 1 \text{ cm}^{-1}$. ^c Absorptions assigned to ionic species are italicized. ^d This compound was prepared by a metal exchange reaction starting with the analogous mercury compound.¹³

$\text{SnMn}(\text{CO})_5$,³ and $(\text{C}_6\text{H}_5)_3\text{SnMo}(\text{CO})_3\text{C}_5\text{H}_5$ ⁴ to mention only a few. In addition to obvious structural relationships, the chemical properties of compounds containing metal-to-metal bonds have been shown to be similar in many ways to those containing well-established metal-to-carbon covalent bonds.⁵

This communication describes the preliminary results of a study of the heterolytic cleavage of transition metal-to-main group metal covalent bonds. Contrary to a previous report concerning $\text{Zn}[\text{Co}(\text{CO})_4]_2$ which stated "Von Wasser wird die Substanz nicht benetzt,"⁶ we have observed that yellow, crystalline $\text{Zn}[\text{Co}(\text{CO})_4]_2$ dissolved readily in deaerated water, without gas evolution, to give a colorless solution. At a concentration of 0.010 *M* the observed molar conductivity of 132 ohm^{-1}

a wide spectrum of behavior is observed. The tetracarbonylcobalt derivatives (1 through 4) were particularly useful in this study because the single well-characterized absorption of $\text{Co}(\text{CO})_4^-$ at 1892 cm^{-1} in DMF⁷ was shifted from absorptions due to undissociated species. In DMF as in water $\text{Zn}[\text{Co}(\text{CO})_4]_2$ dissolved to give a stable (though somewhat air-sensitive) colorless solution. The infrared and conductance data showed that dissociation was essentially complete. As expected the Hg and Cd analogs showed less tendency to ionize. The infrared spectrum of $\text{Hg}[\text{Co}(\text{CO})_4]_2$ in DMF was very similar to that obtained in heptane⁸ and, in agreement with the low conductivity, no absorption due to $\text{Co}(\text{CO})_4^-$ was observed. With $\text{Cd}[\text{Co}(\text{CO})_4]_2$, on the other hand, in addition to the strong anion absorption at 1891 cm^{-1} , bands were observed at 2051 and 1961 cm^{-1} which we attribute to nondissociated or partly dissociated species shifted by strong interaction with the solvent.⁹ It may be noted

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