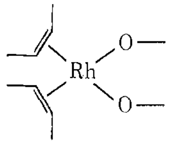
$\times 10^{-12}$ sec; $(C_6H_5)_3CCl$, $\tau = 62 \times 10^{-12}$ sec[12]). Using the data of Table II it is noteworthy that if an atomic polarization of 14 cm^3 is attributed to the rhodium–acac grouping and one of 12.9/2 cm^3 to the olefin–metal bonds, then the total atomic polarization is 20 cm^3 and the dipole moment becomes 0.82 D. Thus it seems reasonable to conclude that the dipole moment of $C_8H_8Rh(acac)$ is 0.9 ± 0.1 D and this result is in accord with the proposed structure B.

Smith and Wilkins[13] have shown that the chemical shifts of the CH and CH_3 protons in the nmr spectra of many acetylacetonates are dependent upon the molecular dipole moment; *e.g.*, in $Sn(acac)_2Cl_2$ for which μ is 8.8 D, the CH chemical shift changes by -0.29 ppm relative to the average nonpolar value of τ, while for $B(acac)F_2$ the CH and CH_3 chemical shifts change by -0.59 and -0.26 ppm, respectively, owing to a dipole moment of 6.7 D. With $C_8H_8Rh(acac)$ the CH and CH_3 proton shifts (τ 4.55 and 8.02, respectively[2]) are not greatly different from the average values found for nonpolar molecules (τ 4.56 and 7.98, respectively[13]) and this is consistent with the small dipole moment observed.

Polarity of the Olefin–Rhodium Bond.—Few data are available on the polarity of olefin–metal bonds and, in particular, there appear to have been no previous studies of the dipole moments of compounds containing olefin–rhodium bonds. If a square-planar arrangement of ligands about the rhodium atom with bond angles of 90° is assumed for structure B (the OMO bond angle is near 90° in most acetylacetonates[14]), then the olefin–rhodium polarity can be calculated provided we have an estimate of the moment of the $C_5H_7O_2Rh$ group. Such an estimate has been given by Coop and Sutton,[8] who successfully used in atomic polarization calculations an experimentally based value of 7.5 D for the moment of an acetylacetonate chelate ring including a metal atom. Use of this value and the experimental resultant moment ($\mu_R = 0.9$ D) leads to two estimates (depending on moment directions) of $\mu(\| \rightarrow Rh)$, 4.7 or 5.9 D. Chatt and Duncanson[15] have proposed that the moment of the olefin–platinum bond is ~4 or 8 D and the former value is favored. The present work indicates that in the olefin–rhodium bond there is a similar large degree of electrical asymmetry and that, as with Pt(II) complexes,[16] back-donation of electrons from the metal to the olefinic bond is probably not a major effect.



$$\mu(\text{acac}-\text{Rh})\text{-}2\mu(\,\| \longrightarrow \text{Rh})\cos 45^\circ = \pm\mu_R$$

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[12] M. Davies, "Molecular Behaviour," Pergamon Press Ltd., London, 1965.

[13] J. A. S. Smith and E. J. Wilkins, *J. Chem. Soc., A*, 1749 (1966).

[14] E. C. Lingafelter and R. L. Braun, *J. Am. Chem. Soc.*, **88**, 2951 (1966).

[15] J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 2939 (1953).

[16] G. T. Behnke and K. Nakamoto, *Inorg. Chem.*, **7**, 2030 (1968).

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Preparation and Some Properties of Tetramethylammonium Dihydrogen Trifluoride[1a]

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In the course of an investigation to develop an electrochemical method of fluorination, the need arose for a fluoride salt soluble in acetonitrile. Tetramethylammonium dihydrogen trifluoride was prepared and it proved to be a useful salt for this purpose.

The preparation of the salt involved treatment of tetramethylammonium chloride with an excess of anhydrous hydrogen fluoride. This procedure is based on the first step in the preparation of tetramethylammonium fluoride described by Urban and Doetzer,[2] in which the hydrogen fluoride bound to the fluoride ion was removed by treatment with sodium ethoxide in methanol, yielding the normal fluoride.

We have found that the removal of excess hydrogen fluoride, without attempting to prepare the normal fluoride, produces a white solid, the composition of which corresponds to $(CH_3)_4NH_2F_3$. With the usual precautions for the exclusion of water, the same composition was observed in five preparations.

It is not surprising that the compound containing $H_2F_3^-$ results from the action of excess HF on $(CH_3)_4NCl$ in view of the high heat of the hydrogen bond in HF_2^-, -37 kcal/mol, reported by Harrell and McDaniel.[3]

Experimental Section

In a typical preparation, tetramethylammonium chloride (Matheson Coleman and Bell, 99+%) was dried at 120° for 12 hr. To 10.04 g (94.0 mmol) of the chloride in a polyethylene beaker 56 ml of liquid hydrogen fluoride was added at room temperature. The fuming mixture was allowed to stand overnight in a hood. When the fuming had subsided (8–12 hr), the beaker and contents were placed in a plastic vacuum desiccator which was attached to a vacuum pump, protected by scrubbers filled with sodium fluoride pellets and a trap at $-78°$. Evacuation was continued until a white solid, mp 103–105°, was formed. A yield of 12.20 g, 95.58%, was obtained. Larger batches of up to 50 g have been made.

Anal. Calcd for $C_4H_{14}NF_3$: C, 36.08; H, 10.60; N, 10.52; F, 42.80. Found (average of elemental analyses[4] of samples from five preparations): C, 35.72; H, 10.38; N, 10.18; F, 42.09.

The HF content of two samples from different preparations was determined by titration with standard sodium hydroxide. *Anal.* Calcd for $(CH_3)_4NF\cdot 2HF$: HF, 30.04. Found: HF, 29.63 and 30.19, which correspond to HF:$(CH_3)_4NF$ ratios of 1.959 and 2.013.

An infrared curve was obtained from the anhydrous salt in a KBr pellet on a Perkin-Elmer Model 421 spectrophotometer.

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[1] (a) Presented at the First Northeast Regional Meeting of the American Chemical Society, Boston, Mass., Oct 1968. (b) NDEA Fellow, 1965–1968. (c) Person to whom inquiries may be directed.

[2] G. Urban and R. Doetzer, German Patent 1,191,813 (April 29, 1965).

[3] S. A. Harrell and D. H. McDaniel, *J. Am. Chem. Soc.*, **86**, 4497 (1964).

[4] Galbraith Laboratories, Inc., Knoxville, Tenn.

A strong absorption peak at 1220 cm^{-1} was attributed to F–H–F bond deformation, similar to the peak at 1233 cm^{-1} in the KHF_2 spectrum of Jones and Penneman.[5] The infrared spectrum of KH_2F_3 reported by Azman, *et al.*,[6] had a series of peaks at 1020, 1050, and 1082 cm^{-1} which they attributed to F–H–F bending. A peak at 1825 cm^{-1} was attributed to H–F stretching, similar to the peak at 1770 cm^{-1} in the spectrum of Azman.[6] Jones and Penneman[5] had observed a peak at 1820 cm^{-1} in solutions of KHF_2 in concentrated aqueous HF and attributed the peak to $H_2F_3^-$ ions. The salt is soluble in water, methanol, ethanol, acetonitrile, and DMF. It is slightly soluble in acetone, pyridine, benzene, carbon tetrachloride, carbon disulfide, and dichloromethane. It is insoluble in cyclohexane and chloroform.

It is not hygroscopic. The assay of a sample, as determined by titration with standard base, changed from 100.5 to 98.75% after standing in air for 36 hr. An infrared curve of a sample left standing in air for 48 hr had no peak which could be attributed to the presence of water.

The voltammetry of a 0.5 *M* solution of the salt in acetonitrile was investigated using a rotating platinum electrode (Sargent Model S-30420) and a saturated calomel reference electrode. The platinum electrode was rotated with a synchronous motor (Sargent Model S-76485) at 600 rpm. The voltammogram was obtained with a Sargent Model XV polarograph, without ir-drop compensation. A useful anodic working range of 0–2.4 V *vs.* sce was observed. This is similar to the range available in solutions of perchlorates in acetonitrile.[7]

The usefulness of the salt for electrolytic fluorination has been demonstrated. Controlled-potential electrolysis of 9,10-diphenylanthracene at 1.65 V *vs.* sce in a 0.4 *M* solution of the salt in acetonitrile produced 9,10-difluoro-9,10-dihydro-9,10-diphenylanthracene[8] in 43% yield.

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[5] L. H. Jones and R. A. Penneman, *J. Chem. Phys.*, **22**, 781 (1954).

[6] A. Azman, A. Oevirk, D. Hadzi, P. A. Giguerre, and M. Schnider, *Can. J. Chem.*, **45**, 1347 (1967).

[7] T. A. Gough and M. E. Peover, "Polarography—1964," Vol. 2, Interscience Publishers, New York, N. Y., 1966, p 1017.

[8] R. F. O'Malley, E. M. McCarron, and C. J. Ludman, submitted for publication.

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Kinetics and Mechanism of the Formation of Nickel(II) and Cobalt(II) Complexes of Glycine and Di-, Tri-, and Tetraglycine in Neutral to Acid Solution[1a]

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Previously, the temperature-jump[2,3] and stopped-flow[4] techniques have been used to determine complexation rate constants for glycine and some oligoglycines with nickel(II) and cobalt(II) ions. The temperature-jump studies are dependent, in part, on independent determinations of the stability constants for these systems. Recent studies have led to a better understanding of[5] and to new stability constants for[6] many of these systems. The stopped-flow technique, on the other hand, is less sensitive to equilibrium data but has been restricted to studies on the formation of the nickel(II) mono complexes, only. In neither case were activation studies carried out.

As a result, we have decided to reexamine the kinetics of nickel(II) and cobalt(II) peptide complexation, including activation studies for the formation of the mono complex of nickel(II). The studies have been carried out at pH's below the narrow region which gives rise to the yellow, diamagnetic complex for nickel;[5,6] therefore, this investigation refers to the so-called octahedral complexes of both metal ions.[7]

Treatment of Data

Relaxation Spectra.—The observed relaxation processes have been assigned to reactions of the type

$$MY_{n-1}^{(3-n)+} + Y^- \underset{k_{-n}}{\overset{k_n}{\rightleftharpoons}} MY_n^{(2-n)+} \qquad (1)$$

In eq 1 $n = 1, 2,$ or 3; the symbol M is Ni or Co; the symbol Y^- represents the anionic form of the ligand, with all peptide nitrogen hydrogens (only glycine is not a peptide) attached. For the sake of convenience a further symbolism will be employed; namely, Y^- is G^- for glycine, HG_2^- for diglycine, $H_2G_3^-$ for triglycine, and $H_3G_4^-$ for tetraglycine. Hydrogens appearing in the G symbolism are bound to a peptide nitrogen.

Neither triglycine nor tetraglycine forms tris complexes.[5] Although glycine and diglycine form three complexes, experimental conditions were chosen so that not more than two reactions were appreciably coupled in any given experiment. Therefore, the general treatment of Hammes and Steinfeld could be applied.[2]

A complication in these studies is the dissociation of peptide hydrogens. In the G symbolism, an example would be

$$Ni(H_2G_3)^+ \rightleftharpoons Ni(G_3)^- + 2H^+ \qquad (2)$$

This process did not interfere with the analysis for two reasons. First, the reactions have been observed to be slow,[8] lying outside the time range of the temperature-jump technique. Second, to ensure (a) that the reactions will indeed be slow and (b) that species such as $Ni(G_3)^-$ will be in the minority, the pH was kept

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[1] (a) The authors gratefully acknowledge partial support of PHS Research Grant GM-08893-07 from the National Institute of General Medical Sciences, Public Health Service, and of the Petroleum Research Fund for Grant 2982B (R. F. P.). (b) Department of Chemistry, Ithaca College, Ithaca, N. Y. 14850.

[2] G. G. Hammes and J. I. Steinfeld, *J. Am. Chem. Soc.*, **87**, 4639 (1962).

[3] J. I. Steinfeld and G. G. Hammes, *J. Phys. Chem.*, **67**, 528 (1963).

[4] J. Cassatt and R. G. Wilkins, *J. Am. Chem. Soc.*, **90**, 6045 (1968).

[5] N. W. H. Ma, D. A. White, and R. B. Martin, *Inorg. Chem.*, **6**, 1632 (1967).

[6] M. K. Kim and A. E. Martell, *J. Am. Chem. Soc.*, **89**, 5138 (1967).

[7] For detailed kinetic data, order Document No. NAPS-00359 from ASIS National Auxiliary Publications Service, c/o CCM Information Sciences, Inc., 22 West 34th St., New York, N. Y. 10001. Remit $1.00 for microfiche or $3.00 for photocopies. Advance payment is required. Make checks or money orders payable to: ASIS-NAPS.

[8] R. G. Wilkins, private correspondence.