iodides, that is, alkyl amines > alcohols > ethers > aromatics > alkanes. The low solubility of the pyridinium salts in poorly solvating liquids requires indirect methods for the assignment of Z values to the very soft donors. By contrast, iodine is particularly attractive as a reference soft acid for determining comparative softness of nonpolar and aprotic donors.

Experimental Section

The 4-carbomethoxy-1-ethylpyridinium iodide (Eastman Organic Chemicals) was recrystallized by dissolving the solid in warm chloroform containing a minimum of added absolute methanol. The filtered solution was allowed to concentrate and crystallize at room temperature, giving yellow-orange crystals (mp 114°). Acetone[5] was not as suitable as a solvent, since it was quite difficult to free the solid product completely from adsorbed solvent, and the solute tended to separate as an oil.

All donor solvents were Spectro-Analyzed reagents with the exception of the amines (Eastman White Label). Solvent Z values were obtained by the procedure of Kosower.[5] However, those for pure *p*-dioxane and tetrahydrofuran were graphically extrapolated from Z *vs.* v/v fraction in binary mixtures with water. Experimental values for chloroform and the amines were measured in binary solutions with added methanol (20% v/v), because of the low solubility of the pyridinium salt. Absorption maxima were determined on a Beckman DU spectrophotometer.

CONTRIBUTION FROM ROCKETDYNE, A DIVISION OF NORTH
AMERICAN ROCKWELL CORPORATION,
CANOGA PARK, CALIFORNIA 91304

Preparation of Chlorodifluoramine, $ClNF_2$

BY KARL O. CHRISTE

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The synthesis of $ClNF_2$ was first reported in 1960 by Petry.[1] Since then, numerous papers dealing with the preparation of this interesting compound have been published.[2-9] The majority of these preparations are based on the reaction of HNF_2 with chlorine or chlorine-containing compounds.[1,4-6,9] With the exception of the reactions between HNF_2 and ClF[9] or inorganic hypochlorites,[6] the yields of $ClNF_2$ (based on HNF_2) are only about 50% or lower. The remaining methods based on N_2F_4,[7,8] NaN_3,[3] or NH_4^+-containing salts[2] result in only moderate yields of $ClNF_2$ or are hard to control. This paper reports a new, more convenient synthesis of $ClNF_2$ from HNF_2 and *t*-butyl hypochlorite.

This reaction produces $ClNF_2$ in quantitative yield (based on HNF_2). In contrast to the reaction between HNF_2 and ClF,[9] it does not require the use of a metal–Teflon vacuum system but can be carried out in a standard all-glass vacuum line. Aqueous solutions of inorganic hypochlorites have previously been used[6] to convert NHF_2 into $ClNF_2$. However, in aqueous solutions proper control of the pH value and use of a flow reactor are essential to suppress the competing reaction resulting in the formation of N_2F_4.

Experimental Section

Caution! Difluoramine is highly explosive[4] and protective shielding should be used during handling operations. The compound was always condensed at −142° and the use of a −196° bath should be avoided.[4]

Materials and Apparatus.—Difluoramine was prepared from difluorourea as reported by Lawton, *et al.*[10] *t*-Butyl hypochlorite was prepared from *t*-butyl alcohol.[11] Both compounds were purified by fractional condensation and their purity was determined by infrared spectroscopy. All reactions were carried out in a Pyrex high-vacuum line having stopcocks lubricated with Halocarbon grease (from Halocarbon Products Corp.). Infrared spectra were taken on a Perkin-Elmer Model 337 spectrophotometer using a 5-cm Pyrex cell fitted with AgCl windows.

Preparation of $ClNF_2$.—Difluoramine (1.06 mmol) and *t*-butyl hypochlorite (1.08 mmol) were combined at −142° in a U trap. The mixture was allowed to warm to room temperature and a smooth reaction took place. After 90 min the mixture was separated by fractional condensation at −54, −95, −142, and −196°. An infrared spectrum of the material trapped at −196 and −142° showed the presence of only $ClNF_2$ (1.06 mmol). The large bulk of the organic material was trapped at −54°.

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CONTRIBUTION NO. 1534 FROM THE CENTRAL RESEARCH
DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT
DE NEMOURS AND COMPANY, WILMINGTON, DELAWARE 19398

A Crystalline Molybdenum(V)–Histidine Complex

BY L. RUSSELL MELBY

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Interest in the implication of molybdenum in enzyme function has prompted recent research on the coordination chemistry of molybdenum ions with α-amino acids, notably cysteine and its esters.[1-3] With respect to other α-amino acids Spence and Lee[4] carried out spectrophotometric, electron paramagnetic resonance, and

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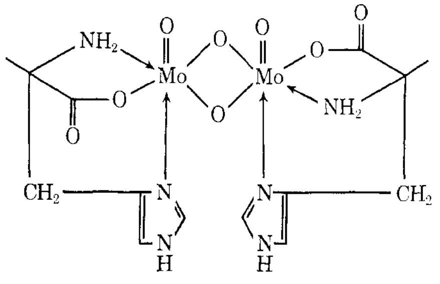
proton magnetic resonance studies of the interactions between L-histidine and molybdenum(V) and molybdenum(VI) in solution. They concluded that at pH 4.6 in water, Mo(V) and histidine interact to form a weak 1:1 complex. Since the complex showed no electron paramagnetic resonance signal, it was presumed to be dimerized or polymerized so as to allow pairing of electron spins of the d^1 Mo(V) ions. However, no other structural conclusions were drawn.

We have now isolated a crystalline molybdenum(V)–L-histidine complex whose gross composition and properties correspond to those described by Spence and Lee. On the basis of elemental analyses, infrared and ultraviolet spectra, optical rotation, and preliminary X-ray analysis, the complex is believed to have a structure, such as **1** or **2**, in which the histidine is tridentate and coordinated with oxygen-bridged Mo(V) ions.[5]



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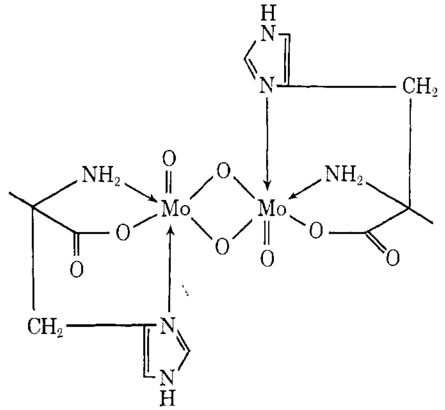

2

The complex was prepared by dissolving molybdenum pentachloride in 3 *N* hydrochloric acid, adding excess L-histidine, and neutralizing the solution with sodium hydroxide. The product separated as shiny amber prisms which retained their shape and luster when air dried but effloresced when vacuum dried.

The complex is diamagnetic in the solid state,[6] and preliminary X-ray analysis indicates a space group of $P2_1/m$ or $P2_1$.[7] The infrared spectrum shows bands assignable to the ligand and oxygen-bridged Mo(V) moiety (Table I). A freshly prepared solution of the complex in deaerated distilled water (pH 4.8) showed an ultraviolet absorption maximum at 297 mμ (ϵ 4000) which decayed and broadened when the solution was exposed to air at room temperature. In the solid state the complex is indefinitely stable in air. When the compound was dissolved in 1 *N* hydrochloric acid, the solution had an optical rotation identical with that of an equivalent concentration of histidine in the same solvent. The ultraviolet absorption spectrum of the acid solution was virtually identical with that of an equivalent concentration of molybdenum pentachloride (λ_{max} 256 and 294 mμ) which is presumably hydrolyzed and dimerized to a binuclear oxygen-bridged species in dilute acid.[8] Thus, in dilute acid the histidine ligands are completely dissociated from the molybdenum. The complex can be regenerated by neutralization of the acid solution.

TABLE I

INFRARED SPECTRUM OF THE MOLYBDENUM(V)–HISTIDINE COMPLEX[a]

Band freq, cm^{-1}		Assignment
3430	s	H_2O
3260 3210	s	NH_2, NH str
1590 1660	vs	COO
941	vs	Mo=O
750	vs	
475	m	MoOMo
450	s	

[a] Nujol mull. See ref 3 for assignment references.

Experimental Section

Methods and Materials.—Infrared and ultraviolet spectra were determined with Perkin-Elmer Model 621 and Cary Model 15 spectrophotometers, respectively.

L-Histidine hydrochloride hydrate was obtained from Cyclo Chemical Corp. and molybdenum pentachloride was from Alfa Inorganics, Inc.

Preparation.—In 20 ml of 3 *N* hydrochloric acid was carefully dissolved 1.35 g (5 mmol) of molybdenum pentachloride and to the warm solution was added 4.2 g (20 mmol) of L-histidine hydrochloride hydrate. While being stirred the deep amber solution was quickly brought to pH 7–8 with 6 *N* sodium hydroxide, and the solution was filtered through a medium-frit funnel. The clear, light amber solution was blanketed with nitrogen; the vessel was capped and allowed to stand overnight to obtain clusters of shiny amber prisms. The product was collected and vacuum dried to obtain 1.2 g of the complex as the dihydrate (80% yield based on molybdenum). Results were similar whether the preparation was carried out in air or under nitrogen. *Anal.* Calcd for $C_{12}H_{16}Mo_2N_6O_8$ (FW = 600.3): C, 24.0; H, 3.3; N, 14.0; Mo, 32.0. Found: C, 23.9; H, 3.1; N, 14.2; Mo, 31.0. In other preparations the elemental analyses varied somewhat, presumably depending upon the degree of hydration.

The product is very difficultly soluble in water and is best recrystallized as follows. In 50 ml of warm 3 *N* hydrochloric acid was dissolved 0.5 g of the complex and the solution was brought to pH 7.5–7.7 with 6 *N* sodium hydroxide and filtered through a fine-frit glass funnel. These operations were conducted in air. The filtrate was seeded with the original compound and blanketed with nitrogen, and the vessel was sealed and allowed to stand undisturbed at room temperature for 1 week to obtain 0.15 g of well-formed prisms.

In 1 *N* hydrochloric acid the complex had a specific rotation $[\alpha]^{24}\text{D}$ +5.5° (*c* 2) compared with +11.5° for L-histidine (*c* 2).

Acknowledgment.—The author thanks Dr. G. W. Parshall for helpful discussions.

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[5] In the analogous 1:1 molybdenum(V)–cysteine complex[2,3] the cysteine is tridentate; see J. R. Knox and C. K. Prout, *Chem. Commun.*, 1227 (1968). Furthermore, histidine is tridentate in bis(histidino)cobalt(II): M. M. Harding and H. A. Long, *J. Chem. Soc., A*, 2554 (1968).

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