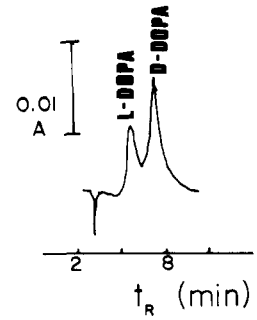

Figure 1. Separation of DL-Dopa on a reversed phase column. The mobile phase is H_2O with 10^{-3} M Aspartame and 10^{-3} M Cu(II). Chromatographic conditions are given in note 17.

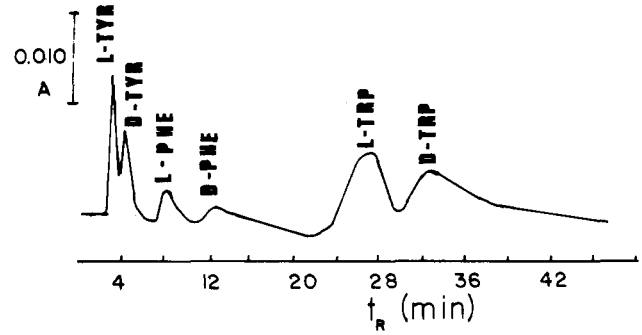

Figure 2. Separation of DL-tyrosine, DL-phenylalanine, and DL-tryptophan on a reversed phase column. The mobile phase is H_2O with 5×10^{-4} M Aspartame and 5×10^{-4} M Zn(II). Chromatographic conditions are given in note 17.

Aspartame, which is an artificial sweetener. (b) The presence of the free α-amino and β-carboxyl groups on the aspartyl residue and a blocked carboxyl group on the phenylalanine residue means that the metal ion is complexed most likely by the aspartylamine and β-carboxyl groups, resulting in a six-membered ring as suggested by Touche and Williams.[16] The ring is less stable than the five-membered ring typical of an α-amino acid–metal complex, allowing the amino acids to be separated more easily from the metal ion. (c) The phenyl group can facilitate the separation via hydrophobic interactions with one isomer of the DL pair. (d) The hydrophobic phenyl and methyl ester moieties allow separation on the usual reversed phase column.

Our intial attempt used a mobile phase consisting of 10^{-3} M Aspartame and Cu(II) in various water–acetonitrile mixtures. DL-tryptophan, DL-phenylalanine, DL-tyrosine, and DL-Dopa were injected into the chromatograph.[17] Table I shows the results of this study. The large α values,[18] which indicate the selectivity of the system, should be noted. As expected, increasing the amount of the organic modifier, acetonitrile in this case, shortens the analysis time. To elute tryptophan in a reasonable time, at least 5% acetonitrile had to be added to the mobile phase. Under all conditions, the L isomer eluted before the D.

To overcome the high detector background signal due to the complex in the mobile phase we have substituted Zn(II) for Cu(II). Table II shows that zinc–Aspartame in the mobile phase can resolve the enantiomers quite successfully. The increase in the retention times and in the selectivities as the amount of zinc(II)-Aspartame is decreased should be noted. A possible explanation of this phenomenon is as follows. If the stationary support is saturated with zinc–Aspartame complex, then the amount of that complex in the mobile phase controls the elution. When the amount of zinc(II)–Aspartame in the mobile phase is decreased, the concentration of the complex adsorbed on the reversed phase increases relative to that in the eluant and the retention time lengthens. This point should be checked further. The retention order is as above: the L isomers elutes before the D. A comparison of Tables I and II shows that, under equivalent conditions, the retention times are longer with the Cu(II) complex.

The examples of the separations are shown in Figures 1 and 2. The former shows the separation of Dopa isomers using copper–Aspartame. Figure 2 demonstrates the separation of the isomers of tyrosine, phenylalanine, and tryptophan with zinc–Aspartame. The chromatographic efficiencies, especially for the strongly retained compounds, are not very good. However, no attempts were made to optimize the system. Some very preliminary results with buffers indicate that the efficiencies can be improved greatly.

Further work in progress shows that the enantiomers of all of the hydrophobic and some polar amino acids can be separated.

Acknowledgments. One of us (E.G.) thanks the National Institutes of Health for the support of this work under Grant No. GM-20846. We thank the Faculty of Natural Sciences of the Hebrew University for the purchase of the liquid chromatograph.

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(17) The chromatographic conditions were as follows: a Spectra Physics chromatograph Model 8000 was used; the column was an ODS one, 25 cm long; the mobile phase flow rate was 2 mL/min; column temperature was 32 °C; detection was done at 275 or 254 nm.
(18) The selectivity factor α is defined as the ratio of the partition coefficients of the solutes of interest; the capacity factor k' is defined as the amount of the solute in the stationary phase proportional to that in the mobile phase. It is directly proportional to the partition coefficient. Large k' values indicate long retention times.

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Preparation and Characterization of an Oxoporphinatochromium(V) Complex

Sir:

Oxometalloporphyrin species have been implicated as intermediates in the catalytic cycles of peroxidases[1] such as horse radish peroxidase and monooxygenases such as cytochrome P-450.[2] Although simple oxometalloporphyrin complexes of vanadium(IV)[3] and molybdenum(V)[4] are known, these compounds do not undergo the oxygen-transfer reactions characteristic of these enzymes. Recently, we reported that chlorotetraphenylporphinatoiron(III) was capable of cata-

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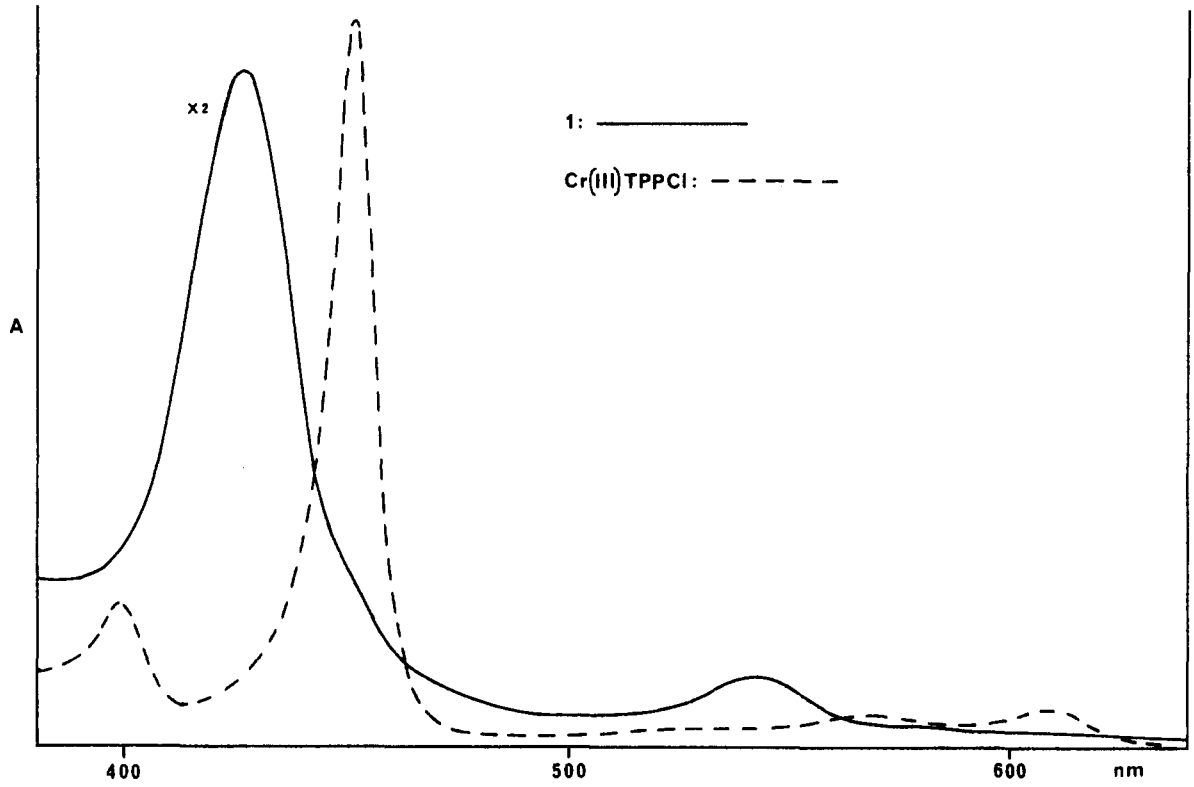
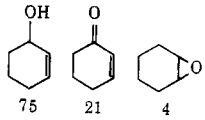
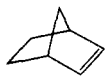
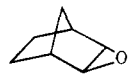


Figure 1. Visible spectra of $Cr^{III}TPPCl$ and **1**.

Table I. Oxidations Catalyzed by Cr^{III} TPPCl–Iodosylbenzene

substrate	products	% yield[a]
	 75 21 4	66
		99[b]
		65
		23
		17
		28
$PhCH_2OH$	PhCHO	56

[a] Yields are based on iodosylbenzene. No other organic products were produced. [b] Contained 3% endo epoxide.

lyzing oxygen transfer from iodosylbenzene to saturated and unsaturated hydrocarbons and suggested the possible intermediacy of an oxoporphinatoiron(V) complex in this reaction.[5] We[6] and others[7] have reported the observation of spectral transients associated with this reaction, but it has not yet been possible to choose among several possible formulations for this intermediate.

We report here the generation and characterization of a stable oxoporphinatochromium(V) complex which is capable of hydroxylating and epoxidizing hydrocarbons under catalytic and stoichiometric conditions.

Chlorotetraphenylporphinatochromium(III) ($Cr^{III}TPPCl$) was prepared and purified according to standard literature procedures.[8] $Cr^{III}TPPCl$ catalyzed the oxidation of simple hydrocarbons with iodosylbenzene giving alcohols and epoxides in fair to excellent yields. Unlike the corresponding iron complexes, $Cr^{III}TPPCl$ also catalyzed the oxidation of alcohols to ketones or aldehydes (Table I).

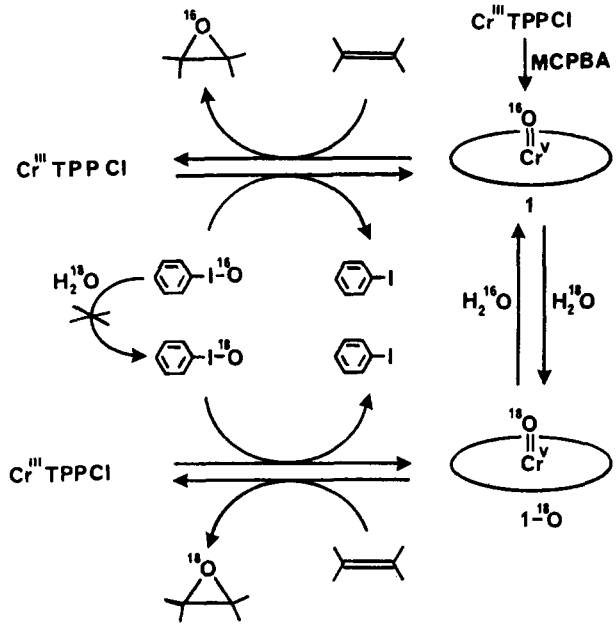
Treatment of $Cr^{III}TPPCl$ with 1 equiv of iodosylbenzene in methylene chloride at room temperature gave a red intermediate, **1**. The same color change occurred upon similar treatment of $Cr^{III}TPPCl$ with *m*-chloroperoxybenzoic acid at −78 °C. The visible spectra of $Cr^{III}TPPCl$ and **1** are compared in Figure 1. Although dilute solutions of **1** in methylene chloride were stable at room temperature for several hours, reaction of **1** with olefins or alcohols caused rapid regeneration of Cr^{III}-TPPCl and oxidation of the organic compound to the same products as those produced in the catalytic reactions.

The infrared spectrum of **1** obtained from iodosylbenzene or MCPBA showed a strong peak at 1005 and a weaker peak at 1026 cm^{-1}. The position of these bands is in good agreement with chromium–oxygen stretching modes of several known oxochromium compounds.[9] The spectrum of **1**-^{18}O, obtained from the reaction of iodosylbenzene-^{18}O (60% ^{18}O)[10] showed diminished intensity at 1026 and a new band at 982 cm^{-1}. Thus, we assign the 1026-cm^{-1} band to a Cr=O stretch in **1**.

Another important aspect of the infrared spectrum of **1** generated from iodosylbenzene was that sharp bands of appropriate intensity at 1018 and 999 cm^{-1}, a characteristic of *free* iodobenzene, appeared in the spectrum. These bands were absent in the spectrum of **1** prepared from MCPBA. Accordingly, the changes observed in the IR spectrum upon reaction of $Cr^{III}TPPCl$ with iodosylbenzene are consistent with discrete oxygen transfer to chromium and release of iodobenzene to the solution. The 1:1 stoichiometry of the reaction and the ^{18}O-dependent Cr=O stretching frequency argue in favor of a formal chromium(V)–oxo complex for the structure of **1**.[11] Alternative formulations of this complex, such as a Cr^{III}–iodosylbenzene complex, can be ruled out on this basis.

The magnetic susceptibility of **1** was compared with that of $Cr^{III}TPPCl$ by the Evans method.[12] The paramagnetic shift

Scheme I



of methylene chloride caused by $Cr^{III}TPPCl$ (8 mg/mL) was found to be 7.4 Hz at 60 MHz. This shift corresponds to an experimental magnetic susceptibility of 3.8 ± 0.2 μ_B, in very good agreement with the theoretical spin-only value of 3.87 μ_B expected for chromium(III). The corresponding paramagnetic shift of **1** (6 mg/mL) was 0.95 Hz which corresponds to a magnetic susceptibility of 2.05 ± 0.2 μ_B. This low value is close to the spin-only magnetic susceptibility of 1.73 μ_B expected for a chromium(V) complex. Partial decomposition of the intermediate in the NMR probe (35 °C) was apparent during the measurement and would account for the small observed discrepancy.[13] Treatment of this solution of **1** with cyclohexanol caused the magnetic susceptibility to increase again to 3.8 ± 0.2 μ_B consistent with the regeneration of $Cr^{III}TPPCl$.

Cytochrome P-450 is known to incorporate one oxygen atom from molecular oxygen into substrate molecules while the other appears as water.[2] It has been observed, however, that the oxidation of cyclohexane by cytochrome P-450 in the presence of $H_2{}^{18}O$ leads to a small but distinct amount (9%) of ^{18}O incorporation into the cyclohexanol.[14] A chemically reasonable explanation is that a transient intermediate in the oxidative cycle undergoes partial exchange of its oxo ligand before oxygen transfer takes place. An intermediate equivalent to FeO^{3+} is an attractive choice[15,16] since oxo-metal complexes are known to undergo oxygen exchange in water.[17]

We have found that treatment of **1** with excess $H_2{}^{18}O$ (95% ^{18}O) caused the disappearance of $\nu_{Cr^{16}O}$ at 1026 and appearance of $\nu_{Cr^{18}O}$ at 982 cm^{-1}. The reaction of this exchanged material (**1**-^{18}O) with norbornylene afforded norbornylene oxide with 94% incorporation of the ^{18}O label. Controls indicated that iodosylbenzene did not undergo oxygen exchange under these conditions.[18] Clearly, the oxo ligand of **1** is labile toward aqueous exchange.

A mechanistic scheme consistent with these observations is presented in Scheme I. The generation of this stable oxochromium(V) complex and the observation that it reacts readily with hydrocarbons and exchanges its oxygen with water provide a significant new precedent for the intermediacy of an oxo-iron intermediate in the cytochrome P-450 cycle as well as in the simple iron-porphine system which we have recently described.[5]

Acknowledgments. Support of this work by the National Institutes of Health (GM25923), the National Science Foundation (CHE-77-21849), and the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged. The National Science Foundation provided funds for the purchase of a GC-mass spectrometer.

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Remarkable Influence of Terminal Alkoxy Groups on Carbonyl Ligands as Seen in the New Compounds $Mo(OBu^t)_2(CO)_2(py)_2$ and $Mo_2(OPr^i)_8(CO)_2$

Sir:

Previously it was shown[1] that hydrocarbon solutions of $Mo_2(OBu^t)_6$ (M≡M) react with CO under very mild conditions (room temperature, ≤1 atmo of CO pressure) according to the stoichiometric reaction shown in eq 1.

$$2Mo_2(OBu^t)_6 + 6CO = Mo(CO)_6 + 3Mo(OBu^t)_4 \quad (1)$$

The first step in reaction 1 is rate determining, reversible, and involves the formation of $Mo_2(OBu^t)_6(\mu\text{-}CO)$ in which the CO ligand bridges a Mo=Mo of distance 2.498 (1) Å; ν(CO) is at 1670 cm^{-1} (Nujol mull) and the Mo-C and the C-O distances are 2.02 (1) and 1.21 (2) Å, respectively.[1]

Although analogous carbonylation of $Mo_2(OPr^i)_6$(M≡M) also yields $Mo(CO)_6$, the stoichiometry of the reaction differs from that in eq 1. The Mo^{4+} isopropoxide is dinuclear, $Mo_2(OPr^i)_8$, and contains a M=M of 2.523 (1) $Å^2$ distance and reacts with CO to form a black, paramagnetic crystalline dicarbonyl compound, $Mo_2(OPr^i)_8(CO)_2$.[3] This compound is not thermally stable toward vacuum sublimation, but did

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