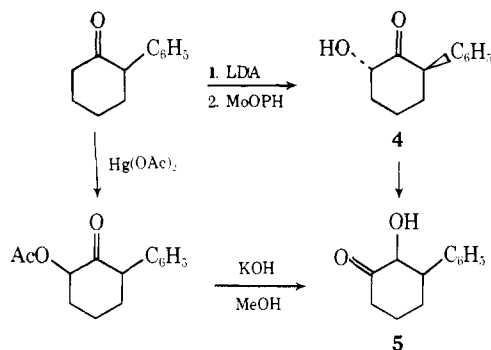


A labile acyloin **4**¹⁴ is formed from 2-phenylcyclohexanone in 70% yield. Structure **4** has previously been assigned to a compound obtained by reaction of 2-phenylcyclohexanone with mercuric acetate followed by saponification of the initial product, 2-acetoxy-6-phenylcyclohexanone.¹⁵ The structure of the acetate is supported by spectral data, but the nmr spectrum of the saponification product can only be reconciled with the isomeric acyloin **5**.¹⁶ Methanolic KOH converts **4** into



5 within minutes at 25°, but **5** is not present in the crude MoOPH product by tlc analysis. Thus, it is possible to prepare the less stable acyloin by hydroxylation of the kinetically favored enolate¹⁷ without interconversion of acyloin isomers.

Numerous synthetic applications are anticipated for transition metal peroxide hydroxylations, including oxidative degradation of esters and ketones and ring expansions of cycloalkane acyloins¹⁹ or of pinacol rearrangement systems²⁰ available from cycloalkane α -hydroxy esters. We are also investigating hydroxylation of other carbanions and the behavior of related metal peroxide reagents.

Acknowledgment. The author wishes to thank the Upjohn Company for steroid samples used in this work.

(14) Noncrystalline, purified by preparative layer chromatography: nmr (CDCl_3 , δ) 7.1–7.6 (5 H, m), 4.18 (1 H, dd, $J = 11, 6$ Hz), 4.03 (1 H, br s), 3.7 (1 H, br s, exchanged by D_2O), 1.4–2.8 (m, 6 H); ir (cm^{-1} neat) 3340 (br), 1720 (s).

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(16) A sample of **5** was prepared by the mercuric acetate-saponification procedure¹⁵: mp 118–119°; nmr (CDCl_3 , δ) 7.24 (5 H, br s) 4.28 (1 H, dd, $J = 12, 1.5$ Hz; 1.5 Hz coupling disappears after shaking with D_2O), 3.6 (1 H, d, $J = 1.5$ Hz; D_2O exchangeable), 1.5–2.9 (7 H, m).

(17) Exclusive (>99%) formation of the less substituted enolate from 2-phenylcyclohexanone and LDA has been verified by Professor H. J. Reich (personal communication). Similar behavior is apparent in the case of acid-catalyzed bromination,¹⁸ as well as the mercuric acetate oxidation.¹⁵

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Received April 22, 1974

Reversible Oxygen Binding by Divalent Chromium(II) Ion Exchanged Molecular Sieve

Sir:

Reversible binding of molecular oxygen by transition metal complexes continues to be of interest and the

subject has recently been reviewed by Valentine.¹ To date iridium,² rhodium,³ palladium, platinum, nickel,⁴ and iron⁵ reversibly formed dioxygen complexes have been reported. In addition there are the numerous reversibly formed dioxygen complexes of cobalt.¹ Though simpler than the hemoglobin molecule whose reversible oxygenation is of prime interest, most, if not all, of these complexes involve extensive covalent binding of the ligands with the central ion, raising the question of the extent to which ligands other than oxygen participate in the binding scheme.

We report on a heterogeneous oxygen carrier based on chromium(II) introduced by ion exchange into a zeolite cavity and coordinated by no ligands other than the zeolite framework.

Exchange of transition metal ions into A type zeolites and subsequent dehydration leaves the exchanged ion in trigonal coordination in a distorted oxygen six ring which links the α and β cages of the zeolite.^{6–8} The ions are coordinatively unsaturated to a high degree, allowing them to bind "guest molecules" which are small enough to enter the zeolite cavities. Examples of zeolitic complexes in which a transition metal ion is bound partly to the zeolitic skeleton and partly to a guest molecule are the olefin and acetylene ($\text{Na}_{0.834}\text{Co(II)}_{0.083}$)-A,⁹ acetylene ($\text{Na}_{0.25}\text{Mn(II)}_{0.375}$)-A,¹⁰ and the water, cyclopropane, and ethylene complexes of ($\text{Na}_{0.715}\text{Ni(II)}_{0.143}$)-A.⁶

Ion exchange of divalent chromium into zeolite A under oxygen-free conditions yielded a pale blue air-stable material containing 1.5 Cr(II) ions per unit cell, ($\text{Na}_{0.75}\text{Cr(II)}_{0.125}$)-A, having a diffuse reflectance electronic spectrum characteristic of the hexaquo Cr(II) ion. Similar behavior was observed for the nickel⁶ and cobalt⁹ exchanged zeolites. Dehydration at 350° and 10^{-6} Torr induced a pale blue-lilac color in the zeolite and an electronic diffuse reflectance spectrum having two peaks (Table I).

Table I. The Diffuse Reflectance Electronic Spectra (cm^{-1}) of Anhydrous and of Oxygenated Anhydrous Chromium(II) Ion Exchanged A Type Zeolite^a

($\text{Na}_{0.75}\text{Cr(II)}_{0.125}$)-A	($\text{Na}_{0.75}\text{Cr(II)}_{0.125}$)-A + O_2
12,300 m	4,000 w
17,000 m	10,000 s, sh
	14,200 s
	18,000 m
	20,600 m
	26,200 w

^a Key: m = medium, w = weak, s = strong, sh = shoulder.

Magnetic susceptibility measurements showed that the chromium ion was in a high spin state ($2S + 1 =$

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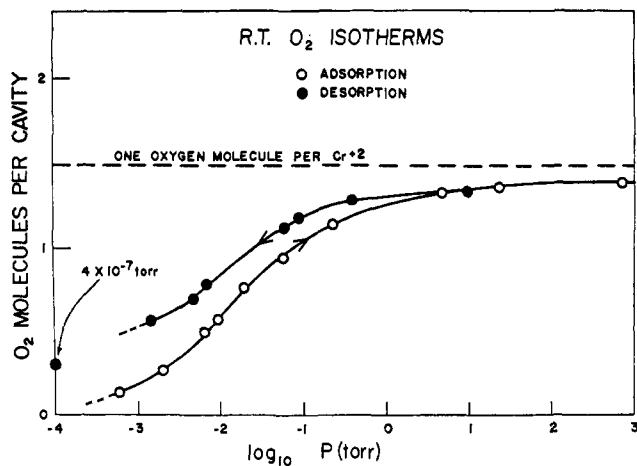


Figure 1. The oxygen chromium(II) exchanged anhydrous zeolite A room temperature isotherm. The adsorption is approximately 80% reversible at room temperature. The oxygen uptake also produces reversible color changes in the sample (see text).

5) with a magnetic moment at room temperature of 5.0 BM. A calculation of the energy levels of a quintet d^4 ion under a D_{3h} ligand field potential has been performed and will be published. Two spin allowed transitions are predicted and the 12,300 and 17,000 cm^{-1} peaks of the anhydrous $(\text{Na}_{0.75}\text{Cr(II)}_{0.125})\text{-A}$ are assigned to the ${}^5E' \rightarrow {}^5E''$ and ${}^5E' \rightarrow {}^5A_1'$ transitions where the states ${}^5E'$, ${}^5E''$, and ${}^5A_1'$ originate by the splitting of the atomic term 5D under the D_{3h} potential. On the basis of the agreement between the experimental and theoretical spectra, the divalent chromium ion is coordinated by the zeolitic oxygen six ring, as are the Ni(II)^{6,7} and Co(II) ions.⁸

X-Ray diffraction patterns of the hydrated and anhydrous chromium(II) exchanged zeolites were compared to the hydrated nonexchanged zeolite pattern and showed that neither the ion exchange nor the subsequent dehydration degraded the zeolitic structure.

Exposure of the pale blue-lilac anhydrous zeolite to dry oxygen at 760 Torr instantly induces a gray color. The diffuse reflectance electronic spectrum of the oxygenated sieve is quite different from that of the nonoxygenated sieve (Table I) indicating a specific interaction between the chromium and the oxygen. This interaction is confirmed by the oxygen adsorption isotherm obtained using a quartz spring microbalance. Figure 1 shows that the uptake of oxygen starts at ca. 5×10^{-4} Torr and that at a pressure of 1 Torr the oxygen molecule-chromium ratio is close to unity. Desorption of the oxygen is affected by reduction of the oxygen pressure above the sample and is accompanied by a return to the blue-lilac color of the nonoxygenated sample.

In accord with the proposed binding schemes for other reversibly oxygenated transition metal complexes,¹¹⁻¹³ we suggest that the oxygen molecule accepts an electron from the rather easily oxidized Cr(II) ion and that the resulting superoxide anion is bound in π geometry to the now formally trivalent chromium ion.

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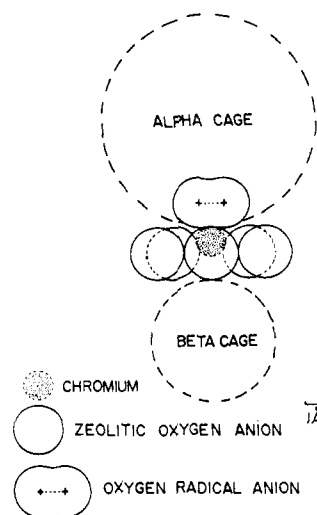
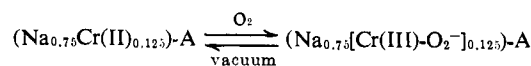


Figure 2. The proposed structure of the anhydrous chromium(II) ion exchanged zeolitic molecular oxygen complex. The figure is drawn to scale. The dimensions of the oxygen radical anion are taken from ref 11. The chromium ion is pulled out of the six ring by the oxygen.



The room temperature magnetic moment of the complex is 3.7 BM, indicating spin pairing between the chromium ion and the oxygen radical anion. This behavior is also typical of transition metal ion-oxygen complexes, many of which are diamagnetic.¹³ On the assumption that the spin pairing arises from weak magnetic interaction and that the chromium in the oxygen complex can be treated as a d^3 ion within the framework of ligand field theory, the electronic spectrum Table I (right) is to be interpreted as that of a d^3 ion under C_{1v} ligand field. Preliminary calculations show reasonable agreement with the observed spectrum. The proposed structure of the complex is given in Figure 2. However, other geometries are not excluded and further experimental data are needed to resolve structural details.

In summary, divalent chromium on anhydrous zeolite A is a particularly simple reversible oxygen binder. The nonoxygenated chromium is coordinated by three zeolitic oxygens and to a good approximation behaves as an ionic complex. No simpler oxygen carrier appears to have been reported.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research.

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Carbonylbis(L-methionine *p*-nitrophenyl ester). A New Reagent for the Reversible Intramolecular Cross-Linking of Insulin

Sir:

The biological synthesis of insulin occurs through a single peptide chain (proinsulin) in which the COOH