in Figure 2 requires equivalence of the cyclopentadienyl groups, which is consistent with the observed NMR spectra.

If $(OC)_4CoGeCl_3$[13] is reacted with $W_{11}SiO_{39}^{8-}$, the anion $[(OC)_4CoGe]_2W_{11}SiO_{40}^{4-}$ is apparently formed initially. This, however, undergoes rapid disproportionation of the type discussed above for $(OC)_4CoSnW_{11}SiO_{39}^{5-}$. In the case of $[(OC)_4CoGe]_2W_{11}SiO_{40}^{4-}$, the presence of two $(OC)_4CoGe$ moieties gives rise to a polymer as the disproportionation product:

$$(OC)_4CoGeCl_3 + W_{11}SiO_{39}^{8-} \rightarrow [[(OC)_4CoGe]_2W_{11}SiO_{40}^{4-}] \rightarrow [(OC)_3CoGe_2W_{11}SiO_{40}^{5-}]_n$$

The presumed structure of the polymer is shown in Figure 3. Light-scattering molecular-weight determinations on the trimethylammonium salt in dimethyl sulfoxide gave an approximate molecular weight of one million. The infrared spectrum was consistent with a t-$L_2CO(CO)_3$ configuration as discussed above for $(OC)_3Co(SnW_{11}PO_{39})_2^{9-}$ and was strikingly similar to that of $W_{12}SiO_{40}^{4-}$ in the 1000–700-cm^{-1} region.

Further physical and chemical characterization of the species described above and extensions of this chemistry to new systems are in progress.

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(6) Typical analyses follow. Calcd (found) for $[(CH_3)_3NH]_4C_5H_5Fe(CO)_2$-$SnW_{11}PO_{39}\cdot 3H_2O$: C, 6.98 (7.05); H, 1.57 (1.51); N, 1.71 (1.74); Fe, 1.71 (1.76); Sn, 3.63 (3.66); W, 61.89 (61.95); H_2O, 1.65 (1.89); CH_3:C_5H_5 proton ratio, 7.2:1 (6.9:1). Calcd (found) for $[(CH_3)_3NH]_{11}(OC)_3Co(SnW_{11}SiO_{39})_2\cdot 4H_2O$: C, 6.69 (6.74); H, 1.86 (1.83); N, 2.38 (2.30); Co, 0.91 (0.86); Si, 0.87 (0.86); Sn, 3.67 (3.47); W, 62.57 (62.62); H_2O, 1.11 (1.24). Calcd (found) for $K_5(OC)_3Co(SnW_{11}PO_{39})Sn(OK)_3\cdot 12H_2O$: C, 0.99 (0.78); H, 0.67 (0.46); Co, 1.62 (1.57); K, 8.60 (8.49); Sn, 6.53 (6.24); W, 55.64 (55.72); H_2O, 5.94 (5.73). Calcd (found) for $[(CH_3)_3NH]_4[C_5H_5Fe(CO)_2Ge]_2W_{11}SiO_{40}$: C, 9.10 (9.06); H, 1.46 (1.53); N, 1.63 (1.61); O, 20.52 (20.51); Fe, 3.24 (3.30); Ge, 4.23 (3.84); Si, 0.82 (1.02); H_2O, 0.0 (0.16); CH_3:C_5H_5 proton ratio, 3.6:1 (3.5:1). Calcd (found) for $\{[(CH_3)_3NH]_5(OC)_3CoGe_2W_{11}SiO_{40}\}_x$: C, 6.59 (6.37); H, 1.53 (1.63); N, 2.13 (2.24); O, 20.98 (20.76); Co, 1.80 (1.92); Ge, 4.42 (4.03); Si, 0.86 (0.93).
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Spectrophotometric Determination of the Proton-Dependent Stability Constant of Ferric Enterobactin

Sir:

Although iron is an abundant element in the earth's crust, the insolubility of ferric ion at physiological pH ($K_{sp} \simeq 10^{-39}$) makes it very difficult for aerobic organisms to acquire the relatively large amounts of iron which they need for growth. In response to this environmental stress, microorganisms have evolved low-molecular-weight chelating agents called siderophores, which solubilize ferric ion and facilitate its transport into the cell.[1] Enteric bacteria such as *Escherichia coli* as well as *Salmonella typhimurium* produce the siderophore enterobactin (H_6ent), shown in Figure 1. It has been known for some time that this compound forms very stable complexes with iron(III). This is indicated by the low pH at which coordination of iron is completed,[2,3] the very low reduction potential of the ferric complex,[4] and the inability of EDTA to remove detectable amounts of iron from ferric enterobactin at pH 7.[5] Although enterobactin has been shown to form octahedral ferric complexes at neutral pH via coordination of the six catecholate oxygens,[6,7] the actual magnitude of the formation constant of ferric enterobactin has never been accurately determined. This datum is of particular importance in relation to current efforts to design specific iron chelators for the iron overload associated with the treatment of β-thalassemia and related human anemias.[8]

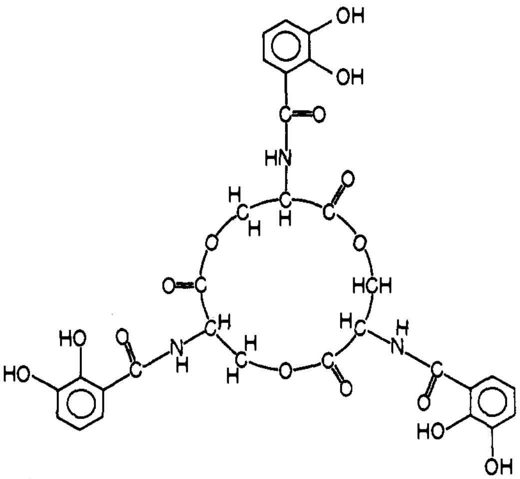

Figure 1. Structural formula of enterobactin.

We report here that the proton-dependent stability constant of ferric enterobactin has been determined spectrophotometrically by competition with EDTA. To do so, it was necessary to take advantage of the sixth-order hydrogen ion dependence of the reaction

$$Fe^{3+} + H_6ent \rightleftharpoons Fe(ent)^{3-} + 6H^+ \tag{1}$$

Even though EDTA is totally incapable of competing with enterobactin for iron at pH 7, a measurable distribution of the metal between these two ligands can be obtained using less than a tenfold excess of EDTA at pH 5. Because the aqueous solubility of enterobactin itself is only approximately 0.1 mM,[9] very dilute solutions (0.08 mM) were used in the competition experiments; the enterobactin was added as 0.3 mL of a concentrated methanol solution, to give a final solution which was 3% methanol by volume.

The stability constant K^* has been determined, where K^* is defined as[10]

$$K^* = \frac{[Fe(ent)^{3-}][H^+]^6}{[Fe^{3+}][H_6ent]} = 10^{-9.7(3)} \tag{2}$$

The ligand protonation constants of enterobactin are still unknown, but, if one assumes typical dihydroxybenzamide values of 8.4 and 12.1 for the two types of ligand -OH groups,[2] the proton-dependent constant, K^*, can be used to estimate the more standard formation constant:

$$K_f = \frac{[Fe(ent)^{3-}]}{[Fe^{3+}][ent^{6-}]} \simeq 10^{52} \tag{3}$$

The visible spectrum of ferric enterobactin has also been recorded as a function of pH, as shown in Figure 2. These data have been used to determine the protonation constant, defined as

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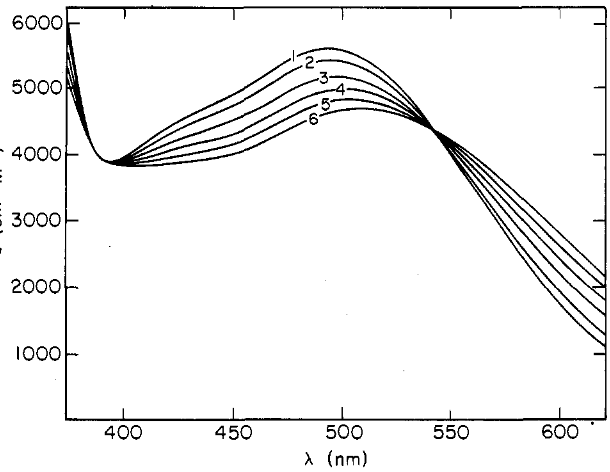

Figure 2. The visible spectrum of ferric enterobactin as a function of pH: 1, 7.29; 2, 5.66; 3, 5.11; 4, 4.80; 5, 4.53; 6, 4.23.

Table I

ligand	log K	log β_3	pM[a]
enterobactin	52		35.5
ferrioxamine B	30.6[b]		26.6
ferrichrome	29.1[b]		25.2
aerobactin	23.1		23.3
tiron		45[c]	19.5
2,3-dihydroxyphenylacetic acid		43.9[c]	15[d]
catechol		43.7[c]	15.8[d]
4-nitrocatechol		43.3[c]	23.4
2,3-dihydroxy-*N*,*N*-dimethylbenzamide		40.2[e]	15[d]

[a] Calculated for 10 μM ligand, 1 μM iron(III), at pH 7.4. [b] $K = [ML]/([M][L])$; values are from ref 11. [c] $\beta_3 = [ML_3]/([M][L]^3)$; values are from ref 3. [d] Calculated pM is below the lower limit determined by the K_{sp} of ferric hydroxide, indicating precipitation of iron under these conditions. [e] Value is from ref 2.

$$K_{\mathrm{Fe(Hent)}} = \frac{[\mathrm{Fe(Hent)}^{2-}]}{[\mathrm{Fe(ent)}^{3-}][\mathrm{H}^+]} = 10^{4.89(6)} \quad (4)$$

This protonation equilibrium was included in the calculation of K^* described above, and its implications will be discussed in a later full report.

The iron(III) stability constants of some hydroxamate siderophores and several bidentate catecholate ligands are listed in Table I. Also listed are pM values (pM = $-\log[\mathrm{Fe(H_2O)_6}^{3+}]$) for iron-ligand solutions at equilibrium under the conditions specified in Table I. The log β_3 values of the catecholate ligands are in the range of 40-45 and are much larger than the formation constants of the hydroxamate siderophores. However, the pM values show that the hydroxamate ligands are much more effective at sequestering ferric ion under the prescribed conditions. This is due primarily to the high basicity of the catecholate ligands, which results in significant competition by hydrogen ion, even at neutral pH. A second factor which is important in dilute solutions is the third-order dependence of β_3 on the free ligand concentration. This reduces the relative effectiveness of bidentate ligands compared with that of compounds forming 1:1 iron complexes.

The log K_f value of enterobactin is the largest formation constant of any iron chelate yet reported and is 7-12 log units larger than the log β_3 values of the bidentate catecholates. Also, since enterobactin forms 1:1 ferric complexes, its effectiveness is not so adversely affected by dilution. As a result of these two factors, the pM value of enterobactin is many log units higher than any of the other ligands listed in Table I. Thus it is clear that enterobactin is a unique and very promising model on which to base future efforts toward the design of more effective iron sequestering agents.

Acknowledgment. This research was supported by the National Institutes of Health (Grant AI 11744).

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Metal Alkyls as Precursors for Polylithium Organic Compounds. A High Yield Synthesis for "C_2Li_6"

Sir:

Polylithium organic compounds have great potential as reagents; more recently, polylithium organic compounds are emerging as one of the most novel and significant areas of investigation with respect to structure and bonding in organic chemistry. We have predicted that the polymeric structures of organic and inorganic polylithium compounds in the solid state may rival the boron hydrides in their complexity and novel bonding properties.[1] The idea that the structures of polylithium compounds as isolated species in the gas phase will be fascinating and most unusual has been more concretely and elegantly illustrated by the ab initio calculations and predictions of Schleyer and Pople and co-workers.[2] Their striking predictions range from bonding configurations of carbon atoms, which are nearly planar rather than tetrahedral, to a number of unusual cases of electron-deficient three-center bonding of lithium and carbon in the monomers. The first structure of a simple polylithium organic compound, "dilithiomethane", is in progress by Stucky and co-workers.[3]

Presently, the elucidation of the structures of polylithium compounds is extremely important. Our synthesis of polylithio compounds using lithium vapor[1,4-7] is complicated by problems in separation of products from the lithium matrix (lithium must be in excess to obtain the most highly substituted compounds) which is always present and from other polylithium species which are generated in the process such as lithium acetylide, C_2Li_2, and byproducts, such as lithium chloride and lithium hydride. A breakthrough in separations of this type is forthcoming.[8] A more difficult problem arises from the fact that, even though yields as high as 90% have been obtained from the lithium reactions,[4] in all previously reported cases the polylithium compounds have been obtained as a mixture of at least three such species. Separation of individual polylithium compounds is a much more demanding problem.

This communication describes a specific high yield synthesis of Li_6C_2 in which the product is obtained in 99% purity from the reaction

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