either $(\eta^5\text{-}C_5H_5)_2Rh_2(CO)_3$ or $(\eta^5\text{-}C_5H_5)Rh(CO)_2$. Thus, although $[(\eta^5\text{-}C_5H_5)Rh(\mu\text{-}CO)]_2$ has for several years been the object of seculation and interest,[17b] it is not surprising that this compound has not been previously observed. The analogous $[(\eta^5\text{-}C_5H_5)Co(\mu\text{-}CO)]_2$ is known to be thermally unstable to give $[(\eta^5\text{-}C_5H_5)Co(CO)]_3$.[10] For both cobalt and rhodium, the $[(\eta^5\text{-}C_5Me_5)M(\mu\text{-}CO)]_2$ complexes, although very sensitive to oxygen, appear to be more robust than their $[(\eta^5\text{-}C_5H_5)M(\mu\text{-}CO)]_2$ analogues.

Assignment of the electronic transition leading to labilization of the CO ligand of $(\eta^5\text{-}C_5H_5)_2M_2(CO)_3$ is not straightforward. Generally, a $\sigma \rightarrow \sigma^*$ absorption is observed for any system that contains a simple 2e metal–metal bond.[1] CNDO calculations performed for $(\eta^5\text{-}C_5H_5)_2Rh_2(CO)_3$ have led to the conclusion that the two highest occupied molecular orbitals are those related to the Rh–Rh and Rh(μ-CO)Rh bonds and that these are very close in energy.[20] Our results suggest that the lowest excited state has substantial M–CO antibonding character. While quantum yields have not been measured, the $(\eta^5\text{-}C_5H_5)_2M_2(CO)_3$ complexes are exceedingly photosensitive. In our hands the complexes are sufficiently photosensitive that their formation cannot be detected upon irradiation of the mononuclear $(\eta^5\text{-}C_5H_5)M(CO)_2$ species in a 93 K methylcyclohexane matrix. Rather, the dinuclear $[(\eta^5\text{-}C_5H_5)M(\mu\text{-}CO)]_2$ species appear to be prompt products. The extreme photosensitivity of $(\eta^5\text{-}C_5H_5)_2M_2(CO)_3$ suggests that their accumulation upon irradiation of $(\eta^5\text{-}C_5H_5)M(CO)_2$ in low-temperature matrices is unlikely. The structural rearrangement necessary to form $[(\eta^5\text{-}C_5H_5)M(\mu\text{-}CO)]_2$ from the tricarbonyl is likely similar to that for the conversion of the trans isomer of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ to $(\eta^5\text{-}C_5H_5)_2Fe_2(\mu\text{-}CO)_3$.[5] It is evident that such rearrangement is possible at very low temperatures. Interestingly, irradiation of $Fe_2(CO)_9$, which is triply CO-bridged,[21] in a low-temperature matrix gives CO loss, but the $Fe_2(CO)_8$ is formed as a mixture of bridged and unbridged isomers.[22]

Acknowledgment. We thank the National Science Foundation for support of this research.

Registry No. $(\eta^5\text{-}C_5H_5)_2Co_2(CO)_3$, 53450-14-9; $(\eta^5\text{-}C_5H_5)_2Rh_2(CO)_3$, 65138-21-8; $[(\eta^5\text{-}C_5H_5)Co(\mu\text{-}CO)]_2$, 58496-39-2; $[(\eta^5\text{-}C_5H_5)Rh(\mu\text{-}CO)]_2$, 82397-01-1; $[(\eta^5\text{-}C_5Me_5)Rh(\mu\text{-}CO)]_2$, 69728-34-3.

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Kinetics of the Reduction of Manganese(III) Myoglobin by Dithionite

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Received May 14, 1985

Due to its stability in the neutral and basic pH ranges, dithionite ($S_2O_4^{2-}$) has been used to study the kinetics and mechanisms of reactions of numerous metalloproteins,[1–6] metalloporphyrins,[7–14] dioxygen,[15] and classical Werner complexes.[16–19] We report the kinetics of reduction of manganese(III)-substituted myoglobin (Mn^{III}–Mb) into its Mn^{II}–Mb form with dithionite. The metalloporphyrin self-exchange rate constants and potentials are used to predict the relative reduction rates of Fe^{III}–Mb and Mn^{III}–Mb by SO_2^-.

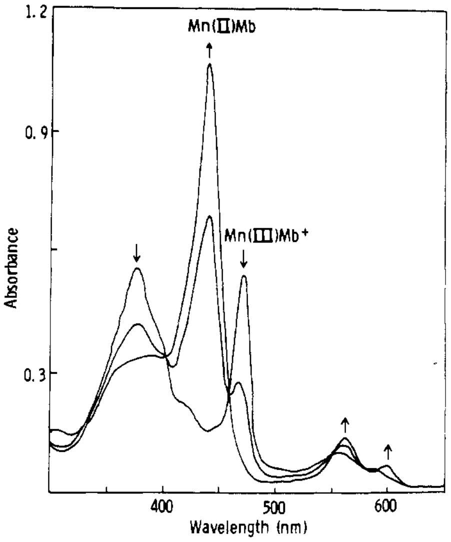

Figure 1. Absorption spectra of Mn^{III}–Mb and Mn^{II}–Mb; pH = 7.

Experimental Section

Manganese(III) myoglobin was prepared from manganese(III) protoporphyrin IX and purified sperm whale metomyoglobin by procedures[20] similar to those used for Co^{III}–Mb[3] and stored frozen at pH 7.3. The absorption bands of Mn^{III}–Mb were essentially the same as those reported by other workers.[21–23] For comparison with Fe^{III}–Mb[4] and Co^{III}–Mb,[3]

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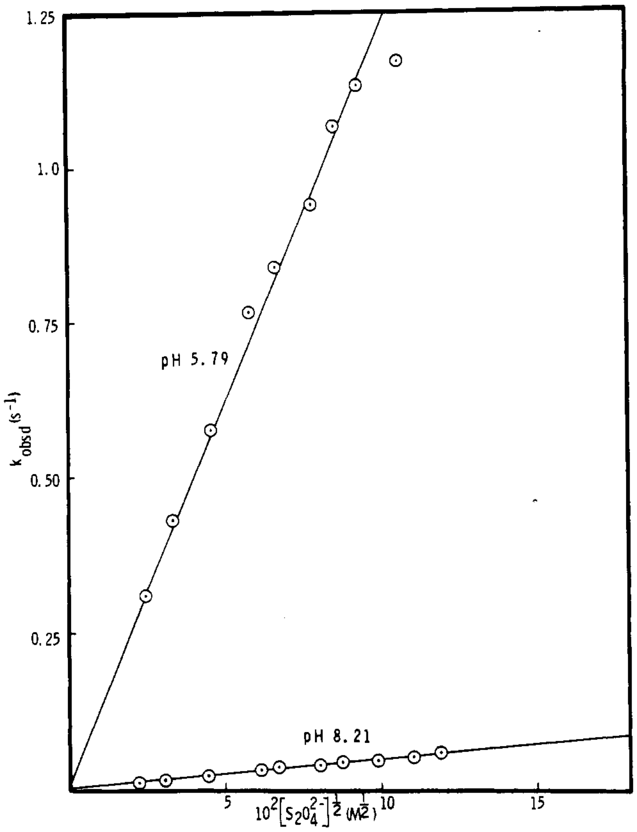

Figure 2. Plot of k_{obsd} vs. $[S_2O_4^{2-}]^{1/2}$ at pH 5.8 and 8.2 for the Mn^{III}–Mb/$S_2O_4^{2-}$ reaction: 25 °C; $I = 0.45$ (Na_2SO_4).

the ionic strength in the kinetic studies was kept at 0.45 (Na_2SO_4) and the solutions were buffered with 10^{-2} M Mes (4-morpholineethanesulfonic acid) between pH 5 and pH 7 and with 10^{-2} M Pipes (1,4-piperazinebis(ethanesulfonic acid)) between pH 7 and pH 8.6. Sodium dithionite was analyzed by titration with ferricyanide.[2] The kinetics were followed at 25 °C on a Durrum-Gibson stopped-flow apparatus, and all reactions were run under chromous-scrubbed argon. Steady-state radiolysis studies[24] using a Gammacell 220 ^{60}Co source were done at pH 7.3 (0.05 M phosphate buffer) in solutions containing 2.5% 2-propanol deoxygenated with N_2O. The $(CH_3)_2COH$ radical is the reductant under such conditions.

Results

Figure 1 shows the spectra of Mn^{III}–Mb and radiolytically produced Mn^{II}–Mb. On the basis of atomic absorption measurements of total manganese, Mn^{III}–Mb has λ_{max} (ϵ, M^{-1} cm^{-1}) at 377 nm (6.5×10^4), 471 nm (6.3×10^4), 555 nm (1.2×10^4), and 590 nm (6.1×10^3). For Mn^{II}–Mb, bands are found at 438 nm (1.3×10^5), 562 nm (1.9×10^4), and 598 nm (1.1×10^4). The same spectral changes were found in the Mn^{III}–Mb/$S_2O_4^{2-}$ reaction above 390 nm, and dithionite itself absorbs strongly below this wavelength. Isosbestic points are at 592, 577, 459, and 399 nm, indicating that Mn^{III}–Mb and Mn^{II}–Mb are the major absorbing species. A spectrophotometric study on Mn^{III}–Mb between pH 5 and pH 8.5 found no change in spectra with pH in this region. When O_2(g) is admitted to the Mn^{II}–Mb solutions, over 97% of the Mn^{III}–Mb spectrum returns, indicating that Mn^{II}–Mb is rapidly oxidized by dioxygen.

Under pseudo-first-order conditions with at least a 100-fold excess of total dithionite over Mn^{III}–Mb, the kinetics of the reduction were first order in Mn^{III}–Mb over 2 half-lives. While most of the reactions were followed at 438 nm, those monitored at 471 nm gave the same observed rate constants, k_{obsd}. The variation of k_{obsd} with dithionite was studied in detail over a 20-fold range in dithionite concentration (1.4×10^{-2} to 4.9×10^{-4} M) at pH 8.2 and over a 20-fold range (1.2×10^{-2} to 6.0×10^{-4} M) at pH 5.8. Figure 2 shows that the reaction is half-order in dithionite at each pH and that $k_{obsd}/[S_2O_4^{2-}]^{1/2}$ increases with a decrease in pH. Figure 3 is the acidity profile of the specific rate from pH 5.3 to pH 8.6. The data could be fitted to eq 1, with A =

$$k_{obsd}/[S_2O_4^{2-}]^{1/2} = (A[H^+] + B)/([H^+] + C) \qquad (1)$$

$1.9_5 \times 10^2$, $B = 1.2_2 \times 10^{-5}$, and $C = 2.5 \times 10^{-5}$. The solid lines in Figure 3 were calculated with these parameters, and the calculated and observed specific rate constants are listed in Table I.

Table I. Observed and Calculated Specific Rates for the Mn^{III}–Mb/$S_2O_4^{2-}$ Reaction[a]

pH	$10^3[S_2O_4^{2-}]$, M	$k_{obsd}/[S_2O_4^{2-}]^{1/2}$, M^{-1} s^{-1} obsd	$k_{obsd}/[S_2O_4^{2-}]^{1/2}$, M^{-1} s^{-1} calcd
5.3	2.1	3.3×10	3.3×10
5.5	3.6	2.1×10	2.2×10
5.7	2.6	1.5×10	1.5×10
5.8	2.6	1.2×10	1.2×10
5.9	2.8	1.0×10	9.8
6.0	2.9	7.5	7.9
6.1	2.9	6.0	6.4
6.3	2.9	4.6	4.3
6.4	2.9	3.2	3.5
6.6	2.5	2.7	2.4
6.7	2.3	1.9	2.0
6.9	2.3	1.6	1.4
7.0	2.3	1.3	1.2
7.1	2.4	1.2	1.1
7.3	2.4	7.6×10^{-1}	8.6×10^{-1}
7.5	2.4	7.2×10^{-1}	7.2×10^{-1}
7.7	2.6	7.5×10^{-1}	6.3×10^{-1}
7.8	2.2	6.0×10^{-1}	5.9×10^{-1}
7.9	2.2	5.8×10^{-1}	5.7×10^{-1}
8.0	2.6	5.1×10^{-1}	5.5×10^{-1}
8.2	2.6	4.9×10^{-1}	5.2×10^{-1}
8.4	2.5	4.7×10^{-1}	5.0×10^{-1}
8.6	2.5	4.7×10^{-1}	4.9×10^{-1}

[a] Conditions: 25 °C, $I = 0.45$ (Na_2SO_4).

Discussion

Manganese(III) porphyrins of varying types have been reconstituted into Mn^{III}–Mb and manganese(III) hemoglobin (Hb), and their relationships to iron and other metal-substituted globins have been explored.[21-23] Both Mn^{III}–Mb and Mn^{II}–Mb are high spin. The lack of dependence of absorption spectra on pH between 5 and 8.5 is in agreement with other studies[21] of Mn^{III}–Mb and certain water-soluble manganese(III) porphyrins,[26] which indicate that H_2O–Mn^{III}–Mb does not form HO–Mn^{III}–Mb below pH 9. While Mn^{III}–Mb binds[21] N_3^-, equilibrium dialysis measurements[3,28] (and spectra[23]) show a lack of rapid interaction with cyanide at pH 7.3. Mn^{II}–Mb complexes[21] with NO(g). Manganese(II) porphyrins under certain conditions[29] carry molecular oxygen. However Mn^{II}–Mb (also Ru^{II}–Mb[30]) is oxidized by O_2 to its 3+ oxidation state.[21-23] La Mar and co-workers[31] have shown that the combination of iron(III) protoporphyrin IX and apomyoglobin produces two protein forms, where the hemin is 180° rotationally disordered about its α,γ-meso axis in the protein pocket. Moreover, different ratios of these forms show differing oxygen affinities.[32] We do not know whether the present Mn^{III}–Mb complex is a mixture of reconstitutional isomers or is present in a single form.

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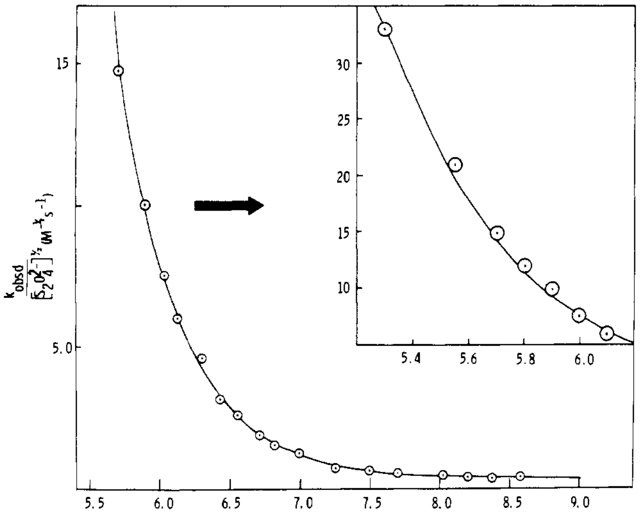

Figure 3. pH profile of the Mn^{III}–$Mb/S_2O_4^{2-}$ reaction. The circles are the experimental points, and the solid lines were calculated from eq 1.

A suggested mechanism for the dithionite reduction of Mn^{III}–Mb is as follows:

$$S_2O_4^{2-} = 2SO_2^- \quad K_D \tag{2}$$

$$Mn^{III}\text{–}Mb\text{–}H^+ = Mn^{III}\text{–}Mb + H^+ \quad K_A \tag{3}$$

$$Mn^{III}\text{–}Mb\text{–}H^+ + SO_2^- \rightarrow Mn^{II}\text{–}Mb + \text{products} \quad k_a \tag{4}$$

$$Mn^{III}\text{–}Mb + SO_2^- \rightarrow Mn^{II}\text{–}Mb + \text{products} \quad k_b \tag{5}$$

With K_D and K_A denoting rapid preequilibria and k_A and k_B the rate-determining steps, the theoretical rate law is as shown in eq 6. By comparison with eq 1, $A = k_AK_D^{1/2}$, $B = k_BK_AK_D^{1/2}$, and

$$k_{obsd} = \frac{(k_AK_D^{1/2}[H^+] + k_BK_AK_D^{1/2})[S_2O_4^{2-}]^{1/2}}{[H^+] + K_A} \tag{6}$$

$C = K_A$. Taking[33] $K_D = 1.4 \times 10^{-9}$ M, $K_A = 2.5 \times 10^{-5}$ ($pK_A = 4.6$), $k_A = 5.2 \times 10^6$ M^{-1} s^{-1}, and $k_B = 1.3 \times 10^4$ M^{-1} s^{-1}. While desirable, it was not feasible to extend the kinetic study below pH 5, as the reduction titer of the dithionite solutions decreased markedly with time in this range. In addition, the K_D determined in base[33] may not be the same in acid, and protonated forms of the reductant might be kinetically important at low pH. Since pHs near the pK_A could not reached, a more conservative estimate is that $pK_A = 4.6 \pm 0.3$ and $k_A = (5 \pm 0.4) \times 10^6$ M^{-1} s^{-1}.

Many experiments on iron and cobalt myoglobin derivatives give evidence for pK_A values in the acid range. In the kinetics of cyanide binding to Fe^{III}–Mb, Ver Ploeg and Alberty[34] found a protein (Fe^{III}–Mb–H^+) pK_A near 6, and Awad and Badro[35] postulate five simultaneous protein ionizations with $pK = 5.6$. Fuchsman and Appleby[36] report a pK of 5.7 from the spectrum of O_2–Fe^{II}–Mb. The O_2–Co^{II}–Mb species shows a pK of 5.6 from visible spectrum changes, 5.3 from EPR hyperfine shifts, and 5.4 from oxygen affinity measurements.[37] Sperm whale myoglobin contains twelve histidine residues,[38] and pK values (which differ depending upon the porphyrin, the iron spin state, and its axial ligands) for a number of histidyl imadazoles, obtained by using ^1H and ^{13}C NMR techniques, have been reported.[38] Three imidazoles are in the porphyrin cavity: the proximal his-93 (F8) bonded to the metal ion, a same-side his-97 (FG3) parallel to the porphyrin plane above ring C, and the distal his-64 (E7), on the opposite side of the porphyrin plane from the other two and near the metal center. For CO–Fe^{II}–Mb, Bradbury and Carver[39] give pK values of 5.0 and 5.9 for distal his-64 and his-97, respectively, and the γ-meso proton of the porphyrin responds to both ionizations with a pK of 5.3. For NC–Fe^{III}–Mb, a number of heme and near-heme protons show[40] a shift of 5.3 ± 0.3, attributed to deprotonation of his-97, for which $pK = 5.6$. Krishnamoorthi and La Mar[41] studied the chemical shifts of the 5-CH_3 porphyrin peak in NC–Fe^{III}–Mbs and found pK's of ca. 5.3 for both native sperm whale Mb and elephant Mb (which has nontitrating glutamine group in place of distal his-64), implicating his-97 as the titrating group in the cavity. They also demonstrated that the pK depends on the nature of the particular 2,4-disubstituted hemin reconstituted in terms of a π–π interaction between the imidazole of his-97 acting as a π donor to the porphyrin π ring system.

Table II. Rate Constants for SO_2^- Reductions of Metalloporphyrins and Metalloproteins

oxidant	k, M^{-1} s^{-1}	ref
Mn^{III}–Mb–H^+	5.2×10^6	tp[a,b]
Mn^{III}–Mb	1.3×10^4	tp
H_2O–Mn^{III}–Hemato[c,d]	5×10^4	8
HO–Mn^{III}–Hemato[d]	1×10^4	8
$(py)_x$–Mn^{III}–Hemato	2×10^6	10
$(py)_x$–Mn^{III}–Proto[c]	5×10^6	10
H_2O–Fe^{III}–Mb[e]	5×10^6	4
HO–Fe^{III}–Mb[e]	3×10^4	4
H_2O–Fe^{III}–Mb[b]	3×10^6	6
NC–Fe^{III}–Mb[e]	2×10^6	4
py–Fe^{III}–Mb[e]	2×10^8	4
H_2O–Fe^{III}–Proto[f]	6×10^6	9
HO–Fe^{III}–Proto[f]	5×10^3	9
$(py)_2$–Fe^{III}–Proto	8×10^7	9
$(NC)_2$–Fe^{III}–Proto	2×10^8	12
$(py)_x$–Co^{III}–Meso[c,g]	4×10^3	10
$(py)_x$–Co^{III}–Deutero[c,g]	8×10^3	10
$(py)_x$–Co^{III}–Br_2Deutero	4×10^4	10
$(NC)_2$–Co^{III}–Proto	1×10^4	11

[a] This paper. [b] Sperm whale myoglobin. [c] The abbreviations are for the 2,4-disubstituted hemato-, proto-, meso-, and deuteroporphyrin IX and dibromodeuteroporphyrin IX. [d] MeOH in H_2O. [e] Horse heart myoglobin. [f] SDS to monomerize porphyrins. [g] 4 M pyridine in water.

We tentatively attribute our pK_A of 4.6 to effects of his-97 in Mn^{III}–Mb. Protonation of this group enhances the Mn^{III}–Mb/$S_2O_4^{2-}$ reduction rate by more than a factor of 300.[42] The rate increase could have an electrostatic component due either to an $-NH^+/SO_2^-$ stabilization in the cavity (if indeed SO_2^- reduces within the cavity rather than at the periphery of the protein[4,5]) or to the relative destabilization of Mn(III) favoring Mn^{II}–Mb due to positive charge accumulation[43] in this crevice. In addition, π donation by unprotonated his-97 would place more electron density on the porphyrin and coordinated Mn^{III}. For a series of manganese(III) porphyrins, it has been shown[10] that the greater the in-plane electron density on the porphyrin, the slower the reduction of Mn^{III}–P by SO_2^-. While it is expected that the Mn^{III}–Mb reduction rates would parallel the $Mn^{III/II}$–Mb reduction potentials at different pHs, such electrochemical data are not available.

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Table II shows a comparison of the reduction rates of several metalloporphyrins and reconstituted metallomyoglobins by dithionite, all of which go by way of SO_2^-. The Fe^{III}–Mb/$S_2O_4^{2-}$ reaction gives a two-term rate law,[4] where SO_2^- reduces H_2O–Mb ($pK_{a1} = 8.9$) several hundred times faster than HO–Mb. The same trend is noted with aquo/hydroxo iron(III) protoporphyrin[9] and aquo/hydroxo cobalt(III) tetrakis(*N*-methyl-4-pyridiniumyl)porphyrin (TMPyP).[13] For manganese(III) hematoporphyrin,[8] $k_{H_2O}/k_{OH} = 3$, and with Fe–CyDTA^{2-} and Fe^{III}–Mb, the ratio[44] is ca. 6. All are consistent with outer-sphere electron transfer and stabilization of the oxidized state by the negative hydroxide.[4,45,46] Co^{III}–Mb (and also low-spin d^6 Ru^{II}–Mb[20] and Rh^{III}–Mb[47]) presumably has both distal and proximal imidazoles coordinated to the metal, and the dithionite reduction kinetics[3] indicated that two such forms (rotational isomers?) were present in the haloprotein. The rate law suggests predissociation of one ligand from Co(III) before reduction of SO_2^-. The Ru^{II}–Mb/CO reaction[30] is also biphasic and dissociative.

At pH 7 with 2.5 mM $S_2O_4^{2-}$, the half-lives for reduction of metallomyoglobins are 9×10^{-2} s for Fe^{III}–Mb,[4] 11 s for Mn^{III}–Mb, and 1.4 and 19 min, respectively, for the two forms[3] of Co^{III}–Mb. For metallomesoporphyrins in pyridine/water, the SO_2^- reduction rates[12] are also in the order Fe > Mn > Co in the ratio 10^4:10^2:1.

Fe^{II}–EDTA at pH 6.8 will reduce Fe^{III}–Mb ($Fe^{III/II}$–Mb, $E°$ = 0.05 V at pH 7), and under similar conditions we find no reduction of Mn^{III}–Mb. This is consistent with the fact that iron(III) porphyrins ($Fe^{III/II}$–TMPyP, $E° = +0.18$ V vs. NHE[48]) have reduction potentials 150–180 mV more positive that the corresponding manganese(III) porphyrin ($Mn^{III/II}$–TMPyP, $E° = -0.01$ V[49]). Mn^{III}–Hb is 122 mV more stable than Fe^{III}–Hb[50] at pH 7. The self-exchange rate constant (k_{11}) for high-spin $Fe^{III/II}$–TMPyP[51] is 1.2×10^6 M^{-1} s^{-1}, and 7.5×10^5 M^{-1} s^{-1} has been estimated for $Fe^{III/II}$–Proto from the Fe^{III}–Proto/$S_2O_4^{2-}$ reaction.[52] The average k_{11} for several manganese(III/II) porphyrins[26] is 2.9×10^3 M^{-1} s^{-1}, where the Fe–TMPyP and Mn–porphyrin results are both based on $Ru(NH_3)_6^{2+}$ reductions. With use of the relative Marcus theory[53] and with the same k_{11}'s assumed for the metalloproteins and metalloporphyrins, the ratio Fe^{III}–Mb/Mn^{III}–Mb for SO_2^- reductions is in the range 10^2–10^3 for differences in potential (ΔE) of 0.1 and 0.2 V. This is in good agreement with the observed (Table II) ratio of 385. From the Fe^{III}–Mb/Fe-EDTA^{2-} reaction,[54] k_{11}^{cor} for $Fe^{III/II}$–Mb = 1.3×10^{-1} M^{-1} s^{-1} (3.9×10^{-2} for Fe–CyDTA^{2-} as the reductant), which is substantially lower than ca. 10^6 M^{-1} s^{-1} for the iron porphyrins themselves. While the rate ratio agreement may be fortuitous, an implication may be that the iron and manganese porphyrin k_{11}'s are lowered to the same relative extent in their metalloglobin forms. Further experiments on this theme are in progress.

Acknowledgment. This work was supported in part by Howard University NIH Biomedical Research Grant 5-SO-6-RR-08016-9 and PHS Grant GM-07700-05 and at the NBS by the Office of Basic Energy Sciences, Department of Energy.

Registry No. $S_2O_4^{2-}$, 14844-07-6; histidine, 71-00-1.

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NMR Study of Carbon-13 in Two Zirconium Iodide Cluster Carbides, $CsZr_6I_{14}C$ and $Zr_6I_{12}C$

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Received March 4, 1985

The inclusion of light nonmetals, carbon especially, in the center of a variety of octahedral M_6X_{12}-type clusters (M = Zr, rare-earth metal; X = Cl, Br, I) has been recently reported.[3-9] The positions of the heavy atoms in the structures of these phases have been well established by single-crystal X-ray diffraction studies. However, the location—indeed the identity and even the presence—of the light nonmetal within the cluster may be more ambiguous in an X-ray study, especially in a compound where the scattering is dominated by the heavier halides and/or secondary extinction effects obscure the presence of the interstitial atom.[9] One example where both of these factors were involved is the misconception of $Zr_6I_{12}C$ as "Zr_6I_{12}".[10,11]

The two phases studied here both contain nominally octahedral clusters of Zr_6I_{12}, the Zr_6I_{14} stoichiometry arising from additional iodine atoms that bridge between the clusters. The X-ray diffraction results show a slightly compressed trigonal-antiprismatic Zr_6 unit (D_{3d} symmetry) in $Zr_6I_{12}C$ (d(Zr–Zr) = 3.35 and 3.28 Å) while in $CsZr_6I_{14}C$ the mode of intercluster bridging produces a tetragonal compression of the cluster but with metal–metal distances of about the same magnitude (3.32 and 3.26 Å), the required C_{2h} symmetry of the metal cluster in fact being rather close to D_{2h}. According to diffraction studies, the carbon (or other) interstitial atom is at the inversion center within each cluster with refined values for d(Zr–C) of 2.259 (1) Å in $Zr_6I_{12}C$ and 2.349 (1) plus 2.265 (1) Å in $CsZr_6I_{14}$. The cesium compound is properly paramagnetic but apparently with an orbital degeneracy such that electron spin–lattice relaxation prevents observation of an EPR signal between 4 and 300 K at 0–13 kG.[9]

To provide information complementary to the X-ray diffraction results, nuclear magnetic resonance spectra of ^{13}C in powdered $CsZr_6I_{14}{}^{13}C$ and $Zr_6I_{12}{}^{13}C$ have been measured. Well-crystallized samples of about 0.4 and 0.2 g, respectively, were prepared as before[9] in virtually quantitative yields from the reaction (850 °C, 2 weeks) of zirconium metal, ZrI_4, CsI (for $CsZr_6I_{14}C$), and 99% enriched ^{13}C graphite in welded Ta tubes that were in turn jacketed in fused silica containers. Both samples were single phase by Guinier powder diffraction, i.e., $\geq \sim 97\%$ pure.

The ^{13}C spectra were all taken at 55.35 MHz on a home-built spectrometer similar to that described previously.[12] Typically, 32 500 accumulations were taken of the free-induction decay (FID) under a single pulse excitation, with appropriate phase cycling (alternate pulses 180° out of phase) to minimize dc offset. The recycle time between scans was 0.2 s. The 90° preparation pulses were 8 μs long.

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[1] Operated for the U.S. Department of Energy by Iowa State University under Contract No. W-7405-Eng-82. This research was supported by the Office of Basic Energy Sciences, Chemical and Materials Sciences Divisions.

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