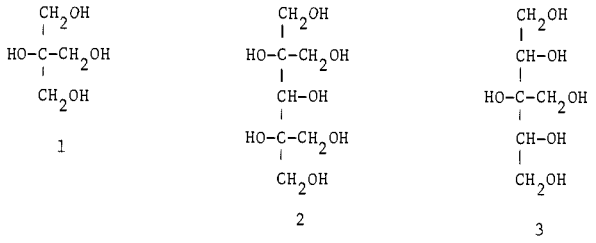

isolated by fractionations with ion-exchange chromatography.[19] Peak 2 product was identified as 2-hydroxymethylglycerol (**1**) by a direct comparison with authentic sample.[20] Peak 26 product was obtained in a crystalline form, mp 117.0 °C.[21] Its ^{13}C NMR spectrum[22] showed a pair of two equivalent CH_2s, a CH, and two equivalent tertiary carbons. The mass spectrum[23] of its trimethylsilyl derivative showed an intense peak at *m/e* 307 compared with peaks at *m/e* 103 and 205 supporting the presence of $-(OH)C(CH_2OH)_2$ group(s) in the parent compound.[24] The results led us to assign structure **2** (2,4-bis(hydroxymethyl)-1,2,3,4,5-pentanepentol) for peak 26 product. Peak 19 product appeared to be a mixture of at least three components. Based on the spectral data,[25] we tentatively assigned this to be a mixture of three diastereomers of 3-hydroxymethyl-1,2,3,4,5-pentanepentol (**3**).

The formation of these branched sugar alcohols may be rationalized by a conventional mechanism[2-4] involving cumulative aldol condensations of formaldehyde followed by cross-Cannizzaro reaction of their aldose precursors. The predominant formation of sugar alcohols instead of aldoses is probably due to enhancement of cross-Cannizzaro reaction at higher pH than that in the usual calcium hydroxide catalyzed formose reaction (near pH 11). To our best knowledge, no one has succeeded to obtain selective formation of particular sugars or sugar alcohols in the formose reaction, except our previous report on the selective formation of **1** and pentaerythritol in a photochemical formose reaction.[20] At moment there is no reasonable explanation for the occurrence of the present selective formose formation. We are undertaking studies toward mechanistic elucidation of the selective formose reaction and a search of other types of selectivity.

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(17) The following selectivities were observed. GLC peak percent for peaks 2, 19, and 26 (total sugar yield in percent): $Mg(OH)_2$, 23, 24, and 42 (46); $Fe(OH)_3$, 16, 19, and 53 (38); FeO, 18, 20, and 39 (35); Al_2O_3, 13, 26, and 23 (32); a control experiment as Figure 1a, 3, 10, and 2 (42).
(18) In a preliminary experiment to search other types of selective reaction, it was found that addition of $Pb_2O(OH)_2$ (lead(II) oxydihydroxide) after the removal of calcium ions at T_{min} resulted in a different selective reaction giving peak 18 product with a GLC PEAK AREA OF 35% and in a total sugar yield of 51%.
(19) The supernatant from the reaction mixture was passed through a IR120(H^+) column and the eluate was repeatedly fractionated on a IRA400(OH^-) column being eluted successively with water and 0.1, 0.5, and 1.0 N KOH.
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(21) Satisfactory microanalytical data for $C_7H_{16}O_7$ were obtained for this compound.
(22) ^{13}C NMR (chemical shifts given in parts per million from Me_4Si and the multiplicities based on an off-resonance spectrum and number of carbon are given in parenthesis): 63.25 (t, 2), 64.71 (t, 2), 72.85 (d, 1), 77.50 (s, 2).
(23) Mass spectrum of the trimethylsilylate: *m/e* 307 (rel intensity 69), 217 (100), 205 (17), 103 (59).
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(25) ^{13}C NMR (see note 22): 62.88 (t), 63.31 (t), 63.73 (t), 64.09 (t), 64.29 (t), 64.76 (t, 3), 70.70 (d), 71.36 (d), 74.47 (d, 2), 76.87 (s), 77.06 (s), 77.85 (s, 1). These signals may be analyzed as those of a mixture of three diastereomers, two meso and a *dl*, of **3**. ^1H NMR of the acetate: δ 2.0-2.2 (m, 18 H), at least 7 CH_3CO peaks), 4.0-4.7 (m, 6 H; CH_2OAc), 5.31 (br t, 2 H, J = 3.5 Hz, $-CH(OAc)CH_2-$). Mass spectrum (rel intensity) of the trimethylsilylate: *m/e* 307 (34), 217 (78), 205 (57), 103 (100).

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Correlation of Electronic Spectra of Metalloporphyrins and Metalloproteins

Sir:

The visible and ultraviolet spectra of metalloporphyrins and metalloproteins have been extensively used in structural determinations and to follow conformational and chemical transformations. There have been several studies concerning the effect of axial ligation on the optical transitions.[1-3] Of the three kinds of interactions—metal-porphyrin, metal-ligand, and ligand-porphyrin—the stereoelectronic effect of ligand on the π orbitals of porphyrin is thought to be most important. The result is a red shift of the Soret band while the effect on the α and β bands is either a hyposochromic or bathochromic one. However, these studies are often complicated by not knowing with certainty whether the metalloporphyrin has one or two axial ligands.

Recently, several laboratories have synthesized and characterized metal-substituted hemoglobins.[4-10] The reduced state metal ion is five coordinated with His F8 as the axial ligand; the metal ion is six coordinated in the oxidized state with either H_2O or an anion as the second axial ligand. We have now synthesized many metal-substituted cytochromes *c*. The cobalt,[11,12] copper,[13] nickel,[14] and zinc[15] derivatives are all six coordinated; one of the axial ligand in these compounds is His 18 while the second axial ligand is Met 80.[12,16] The only exception in this series appears to be the manganese cytochrome *c*[17] which is five coordinated. The purpose of this communication is to show definitive correlation of electronic transition energies with axial ligation in metalloporphyrins.

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Table I. Visible Spectra of Metalloporphyrins and Metalloproteins

Compd[a]	Solvent	α		β				Soret		Ref
		λ (ε)[b]	Δν[c]	λ (ε)	Δν	$\nu_\beta - \nu_\alpha$[d]	Δν̄[e]	λ (ε)	Δν	
Co-OEP	Vapor	554		525		998		382.5		18
Co-OEP	Benzene	552.5	50	519	220	1168	135	394	−763	18
Co-Hb	pH 7	552 (17)	66	523 (sh)	73	1005	70	402 (110)	−1268	6
Co-cyt *c*	pH 7	549 (11.6)	165	520 (9.1)	183	1016	174	416.5 (128.7)	−2134	11
Cu-OEP	Vapor	566		531		1164		387.5		18
Cu-OEP	Benzene	561.5	141	525	216	1239	74	398.7	−726	18
Cu-PPIX·py	Toluene	573	−216	536	−175	1205	−196	408	−1296	13
Cu-cyt *c*	pH 7	577 (9.6)	−337	545 (12.9)	−483	1018	−410	422 (138)	−2109	13
Ni-OEP	Vapor	558		522		1236		384.5		18
Ni-OEP	Dioxane	551 (33.1)	228	516 (11)	223	1231	226	391 (219)	−432	21
Ni-PPIX	MTE	562	−127	524	−73	1290	0	402	−1132	14
Ni-PPIX·py_2	py	566	−253	528	−217	1272	−235	431.5	−2833	14
Ni-cyt *c*	pH 7	578 (5.6)	−620	545 (11.2)	−192	1048	−714	425 (150.6)	−2478	14
Zn-OEP	Vapor	572		535		1209		388.5		18
Zn-OEP	Dioxane	572 (24.5)	0	536 (22.9)	−35	1084	−62	407 (417)	−1170	21
Zn-Hb	pH 7	587 (6.8)	−447	550 (8.4)	−509	1146	−478	423 (122)	−2099	22
Zn-cyt *c*	pH 7	585 (7.9)	−389	549 (15.5)	−477	1121	−433	423 (243)	−2099	15
Mn-OEP	Vapor	574.5		542.5		1027		400.5		18
Mn-OEP·py_2	CH_2Cl_2	581	−194	547	−151	1070	−172	418	−1046	18
Mn-(*meso* PIV DME)py_2	py/H_2O	581 (8.3)	−194	549 (16.5)	−218	1003	−206	426 (158)	−1494	21
Mn-Hb	pH 7	585	−312	555	−415	924	−363	434 (152)	−1927	23, 24
Mn-cyt *c*	pH 7	584 (9.6)	−283	552 (15.3)	−317	993	−299	425 (132.8)	−1440	17
Co-(OEP)$^+Br^-$·py	Benzene	568 (11.7)		537 (13.2)		1016		427 (95)		18
Co-Hb^+	pH 7	572 (9.0)		538 (9.0)		1104		426 (99)		6
Co-cyt c^+	pH 7	567 (7.77)		530 (6.1)		1231		426 (106)		11
Mn-(OEP)$^+Cl^-$	Oil	591		561		905		473.5 360		18
Mn-Hb^+	pH 7	558		550				468 373		23
Mn-cyt c^+	pH 7	548 (10.8)		538 (9.6)		339		461 370		17
Fe-OEP$^+Cl^-$	CH_2Cl_2							378		18
Fe-Hb^+·H_2O	pH 6.4	631 (4.4)		500 (10.0)		4152		405 (179)	−1764	25
Fe-Hb^+·F^-	pH 7.0	605 (10.9)		483 (10.3)		4175		403 (144)	−1641	25
Fe-Hb^+·OAc^-	pH 7.0	620 (5.5)		497 (10.5)		3992		404 (178)	−1702	25
Fe-Hb^+·HCO_2^-	pH 7.0	620 (5.8)		496 (9.2)		4032		404 (178)	−1702	25
Fe-Hb^+·CN^-	pH 7.0		540 (12.5)					419 (124)	−2589	25
Fe-Hb^+·N_3^-	pH 7.0	575 (9.9)		540 (128)		1128		417 (134)	−2474	25
Fe-cyt c^+	pH 7.0	558 (sh)		530 (11.0)		947		410	−2065	26
Fe-OEP	Vapor	563.5		540		772		410.5		18
Fe-OEP	CH_2Cl_2	556	240	531	314	846	277	405.5	+300	18
Fe-OEP·py_2	CH_2Cl_2	543	670	512	1013	1115	842	408	+149	18
Fe-OEP·py_2	py	548 (19.9)	502	518 (14.2)	787	1057	644	400 (125)	639	21
Fe-Hb	pH 7	555 (12.5)	272	523 (sh)	602	1102	437	430 (133)	−1105	11
Fe-cyt *c*	pH 7	550 (29.5)	436	520	713	1049	574	416 (129.1)	−323	26

[a] OEP = octaethylporphyrin, Hb = hemoglobin, cyt *c* = cytochrome *c*, PPIX = protoporphyrin IX, py = pyridine, MTE = methylthioethanol. [b] Absorption maximum, nm (extinction coefficient, mM^{-1} cm^{-1}). [c] Shift from band in vapor phase, cm^{-1}. [d] Separation of α and β bands, cm^{-1}. [e] Shift of the center of the αβ bands from that in vapor phase, cm^{-1}.

Table I summarizes known spectral data on metal-substituted metalloproteins along with some results on metalloporphyrins. The vapor phase spectra of metallooctaethylporphyrins[18,19] serve as reference states free of axial ligands. These spectra were obtained between 300 and 400 °C. The increase of temperature has been shown not to affect the Soret band but shifts[20] the visible bands 5–7 nm to the red, or about −200 cm^{-1}.

We first consider the group of divalent Mn, Co, Cu, Ni, and Zn complexes whose spin multiplicity is not affected by ligation (group A). The first axial ligand shifts the Soret band by -1286 ± 150 cm^{-1}; the second axial ligand causes a shift of -2331 ± 360 cm^{-1}. The ± sign here indicates the range of shifts and is not the standard deviation. According to this criteria, Mn-cyt *c* is the only five-coordinated metal-substituted cytochromes *c*. This is consistent with all the observed properties of Mn-cyt *c* such as EPR spectra, half-reduction potential, and ease of autoxidation and of reaction with nitric oxide. The Soret red shifts also suggest that Zn-Hb is six coordinated and that Mn-Hb is under some influence of a second axial ligand, which is likely to be the distal His E7.

The separation of the α and β bands is insensitive to axial ligation which all lie between 1000 and 1300 cm^{-1} (Table I, column 7). The visible bands appear to be blue shifted for Co proteins but red shifted in the other cases. This discrepancy is removed by taking into account the temperature effect mentioned above. By subtracting 200 cm^{-1} from all of the values in columns 4, 6, and 8 of Table I, one obtains red shifts in all compounds. With the exception of Co, the other metal ions of this group are red shifted from 1.5–2 times greater with two axial ligands than with one ligand, Co being an exception for which the opposite is true.

The α and β bands are assigned by Gouterman and coworkers[27] to be the Q(0-0) and Q(0-1) bands, respectively of the $a_{2u}(\pi) \rightarrow e_g^*(\pi)$ transitions; the Soret band is the 0-0 band of the $a_{1u}(\pi) \rightarrow e_g^*(\pi)$ transitions. Figure 1 shows the destabilization of the $a_{1u}(\pi)$ and $a_{2u}(\pi)$ orbitals by stereoelectronic repulsion due to axial ligands.[28]

The effect of noncomplexing solvent is to shift the Soret band by −400 to −1200 cm^{-1}; i.e., it can be as much as that

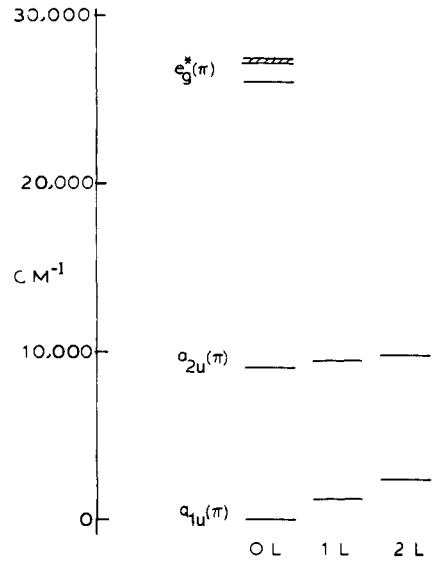

Figure 1. Effect of axial ligation on the energies of the porphyrin π orbitals for group A divalent metalloproteins.

due to a Lewis base axial ligand. Again taking into account the 200-cm^{-1} red shift of the reference compound's visible bands due to temperature, solvents have no effect on these bands of some complexes such as Co- and Ni-OEP but cause about -100 to -300-cm^{-1} shift in Cu and Zn porphyrins.

We consider next the group A trivalent metalloporphyrins and metalloproteins. The cobalt(III) complexes in Table I have nearly identical Soret band frequencies; the center of the visible bands also lie within 260 cm^{-1} of each other. They are all six-coordinated complexes. Manganese(III) complexes have split Soret bands. The long-wavelength band is blue shifted by $\sim$400 cm^{-1} in Mn-Hb^+ and Mn-cyt c^+, while the short-wavelength band is red shifted by $\sim$850 cm^{-1}. So the two Soret bands are $\sim$1250 cm^{-1} closer together than in the manganese(III) porphyrin. The midpoints of the two Soret bands of these manganese(III) compounds differ by $<$300 cm^{-1}. It seems that the Soret band is not significantly shifted by axial ligands for cobalt(III) and manganese(III) porphyrin complexes.

Iron porphyrins and heme proteins differ from those of group A above in that the spin multiplicity of iron and/or its out-of-plane displacement depend upon axial ligation. Consequently, their stereoelectronic spectral shifts should reflect these complications. For instance the Soret red shift by one axial ligand in deoxyhemoglobin is *greater* than by two axial ligands in ferrocytochrome *c*. Furthermore, the visible bands are *blue* shifted by +237 cm^{-1} in Fe-Hb and +274 cm^{-1} in F-cyt *c*. For the iron(III) porphyrins there is no vapor phase spectrum to make comparisons. Instead we compare the spectra of methemoglobins[25] and ferricytochrome *c* with that of Fe-OEP$^+$Cl$^-$ in CH_2Cl_2. High-spin methemoglobins have Soret bands shifted by about -1700 cm^{-1}; the low-spin methemoglobins have greater red shifts of -2100 to -2600 cm^{-1}. This indicates greater stereoelectronic effects in the latter because the Fe atom is in-plane[29] and His F8 lies closer to the porphyrin plane than in the high-spin species. The center of the visible bands are all situated at 18270 $\pm$ 346 cm^{-1}. However, the separations between the α and β bands are much greater in the high-spin methemoglobins ($\sim$4100 cm^{-1}) than the low-spin methemoglobins and ferricytochrome *c*, which are normal.[30]

In conclusion the following rules for stereoelectronic shifts by axial ligation for metalloporphyrins and metalloproteins are proposed. (1) For group A divalent metals, the Soret and the center of the visible bands are shifted by -1286 ± 150 cm^{-1} and -410 ± 20 cm^{-1}, respectively, by one axial ligand; the corresponding shifts are increased to -2331 ± 360 cm^{-1} and -760 ± 150 cm^{-1} by two axial ligands. The separation of the α and β bands are not sensitive to axial ligation. (2) For group A trivalent metals, the Soret band remains the same for different complexes; the visible bands can be either red or blue shifted. (3) For iron(III) complexes the Soret red shift is about -1700 cm^{-1} for high-spin species; it is -2350 ± 250 cm^{-1} for low-spin species. The α and β bands are separated four times greater in the high-spin species. (4) The Soret bands of iron(II) species are red shifted *less* by two axial ligands than by one, whereas the visible bands are blue shifted. It is important to note that the rules are referenced to the vapor spectra of metallooctaethylporphyrins.

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