primarily V in character. The appearance of these three bands is incompatible with the alternative closed-shell ground state, $1\delta_g{}^4$. The strong band at 8.3 eV is assigned to the $2\pi_g$ and $1\pi_u$, primary components of the $\mathrm{Cp}\rightarrow\mathrm{V}$ bond. Although these bonds would also have sextet and quartet components, the multiplet splitting is too small to resolve. The fifth band, which shifts IE substantially when benzene is replaced by mesitylene, is assigned to ionizations from the $1\pi_g$ MO which contains substantial arene π character. The ionizations above about 11 eV correspond to ionizations of C–C and C–H σ bonds and the totally symmetric π ligand combinations, the $1\sigma_g$, $1\sigma_u$, and $2\sigma_u$.

The stability of these 26-electron, open-shell, triple-decker sandwiches suggest a rich chemistry for systems with fewer than 30 electrons! These particular vanadium complexes should have both stable anions with 27 and 28 electrons and possibly stable cations with 25 and 24 electrons. It is conceivable that one could prepare a closed-shell triple-decker sandwich with as few as 22 electrons. Although our description of the bonding is similar, the order of our upper valence orbitals differs from that of Lauher et al.,[1] whose order is incompatible with the photoelectron spectra.

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Registry No. CpV(μ,η^6-C_6H_6)VCp, 86409-35-0; CpV(μ,η^6-$C_6H_3Me_3$)VCp, 86374-48-3.

Synthesis and Structure of Bis(mercapto)cobalt(III) Porphyrins. Models for the Active Site of Cytochromes P450

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Abstract: Reaction of 222-cryptated sodium 2,3,5,6-tetrafluoro- and 2,4,5-trichlorobenzenethiolates with chlorocobalt(III) *meso*-tetraphenylporphyrin in chlorobenzene affords the corresponding bis(thiolato)cobalt(III) *meso*-tetraphenylporphyrin complexes. The crystal structure of the 2,3,5,6-tetrafluorobenzenethiolate derivative $[Co(SC_6HF_4)_2(TPP)][Na\subset 222]\cdot C_6H_5Cl$ (**1a**) has been determined. The crystal structure of a similar complex, $[Co(SC_6HF_4)_2(TPP)][Na\subset 222]\cdot {}^1/_2C_6H_5Cl$ (**1b**), obtained by reaction of O_2 in chlorobenzene with the five-coordinate cobalt(II) derivative $[Co(SC_6HF_4)(TPP)][Na\subset 222]$ has also been studied: **1a**, triclinic, $a = 13.053$ (5) Å, $b = 25.034$ (9) Å, $c = 12.176$ (5) Å, $\alpha = 103.56$ (2)°, $\beta = 110.57$ (2)°, $\gamma = 82.03$ (2)°, $U = 3614$ Å^3; **1b**, triclinic, $a = 15.963$ (6) Å, $b = 16.007$ (6) Å, $c = 14.806$ (6) Å, $\alpha = 108.10$ (2)°, $\beta = 99.31$ (2)°, $\gamma = 91.41$ (2)°, $U = 3537$ Å^3. The octahedral coordination group has an average equatorial Co–N_p distance of 1.977 (4) Å in **1a** and 1.973 (4) Å in **1b**. The effect of the porphyrin conformation on the Co–N_p distances is discussed, and the orientation and structure of the axial ligands are described. These complexes present in solution and in the solid state d hyperporphyrin type spectra. These spectral properties are similar to those of the species obtained by treatment of the native state of cobalt-substituted cytochrome $P450_{CAM}$ with dithiothreitol.

Substitution of iron by cobalt in cytochrome $P450_{CAM}$ has been carried out recently.[1] The EPR spectra of the cobaltous and the oxygenated cobaltous protein indicate an axial ligand other than a nitrogenous base and support sulfur–cysteinate axial ligation. Treatment of the cobalt analogue of $P450_{CAM}$ in the resting state with dithiothreitol leads to a species presenting a d-type hyperspectrum with a red-shifted Soret band at 464 nm and a near-UV band at 374 nm to which there is no precedent for in cobalt porphyrin systems.

Using weakly reducing alkali metal thiolates, we have recently shown that the spectral characteristics (UV–visible–EPR) of the reduced and reduced oxygenated Co $P450_{CAM}$ are "mimicked" by five-coordinate (thiolato)- and six-coordinate oxygenated (thiolato)cobalt(II) porphyrins.[2] We show now that the d-type hyperspectrum obtained by treatment of the resting state of Co $P450_{CAM}$ with a thiol is also mimicked by simple six-coordinate (dithiolato)cobalt(III) porphyrins. We present here the synthesis of two such compounds, their UV–visible spectral characteristics, and two X-ray structures of such a derivative.

Experimental Section

All experiments were done under an inert atmosphere by either Schlenk techniques or in a Vacuum Atmospheres drybox unless otherwise stated. Solvents were rigorously purified and dried under argon. The free tetraphenylporphyrin[3] and its cobalt(III) chloro complex[4] were prepared by published methods. 2,4,5-Trichlorobenzenethiol and 2,3,5,6-tetrafluorobenzenethiol were obtained from Aldrich. The sodium salts were prepared by reacting the thiols and NaH in dry doubly distilled THF and precipitated with pentane. The 222 cryptand (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane) was obtained from Merck.

UV–visible spectra were measured on a Cary 210 spectrometer. Solid-state spectra were obtained on samples deposited as thin films on a face of a cell equipped with a gas inlet.

Synthesis and Crystallization of $[Co(SC_6HF_4)_2(TPP)][Na\subset 222]$ (1). To a solution of $[Co^{III}(Cl)(TPP)]$ (50 mg) in 30 mL of chlorobenzene was added after filtration a chlorobenzene solution (20 mL) of sodium 2,3,5,6-tetrafluorobenzenethiolate (101 mg) and cryptand 222 (150 mg). The mixture becomes slowly green. UV λ_{max} (log ϵ_M): 384 (4.28), 465 (4.46), 532 (3.21), 587 (3.31), 634 (3.47) nm.

1 can be precipitated from this green solution by addition of pentane. The bulk sample obtained in this way is, however, always contaminated by free sodium thiolate. Crystals of $[Co(SC_6HF_4)_2(TPP)][Na\subset 222]\cdot C_6H_5Cl$ (**1a**) were obtained by slow diffusion of pentane (75 mL) to this green solution. UV(solid state): 388, 470, 589, 639 nm. **1** can also be prepared by O_2 oxidation of a chlorobenzene solution of the five-coordinate cobalt(II) complex $[Co^{II}(SC_6HF_4)(TPP)][Na\subset 222]$.[2,5] Slow

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Table I. X-ray Experimental Parameters

	1a	**1b**
formula	$CoClS_2NaF_8O_6N_6$-$C_{80}H_{71}$	$CoCl_{0.5}NaF_8O_6N_6$-$C_{77}H_{68.5}$
mol wt	1546	1506
crystal system	triclinic	triclinic
a, Å	13.053 (5)	15.963 (6)
b, Å	25.034 (9)	16.007 (6)
c, Å	12.176 (5)	14.806 (6)
α, deg	103.56 (2)	108.10 (2)
β, deg	110.57 (2)	99.31 (2)
γ, deg	82.03 (2)	91.41 (2)
U, Å^3	3614	3537
Z	2	2
D_{calcd}	1.42	1.41
μ, cm^{-1}	35.48	36.11
space group	$P\bar{1}$	$P\bar{1}$
radiation	Cu (graphite monochromated)	Cu (graphite monochromated)
crystal size, mm	0.440 × 0.194 × 0.160	0.280 × 0.280 × 0.200
diffractometer	Philips PW 1100/16	Philips PW 1100/16
scan mode	θ/2θ flying step-scan	θ/2θ flying step scan
Δθ, deg	0.90 + Cu $K\alpha_1,\alpha_2$ splitting	0.90 + Cu $K\alpha_1,\alpha_2$ splitting
step width, deg	0.04	0.05
scan speed, deg s^{-1}	0.02	0.02
θ limits, deg	5/57	5/57
no. of data measured	10074	11612
no. of observed data ($I > 3\sigma(I)$)	6317	7312
abs$_{min}$ and abs$_{max}$	35.60/61.45	34.28/48.51
R_1	0.089	0.073
R_2	0.132	0.110

diffusion of pentane to these solutions led to crystals of composition $[Co(SC_6HF_4)_2(TPP)][Na\subset 222]\cdot{}^1/_2C_6H_5Cl$ (**1b**). UV (solid state): identical with **1a**.

Obtaining the two different crystal forms **1a** and **1b** is most probably due to slightly different crystallization conditions.

Synthesis and Crystallization of $[Co(SC_6H_2Cl_3)_2(TPP)][Na\subset 222]$ (2). This compound was prepared with use of the procedure described above with substitution of sodium 2,3,5,6-tetrafluorobenzenethiolate for sodium 2,4,5-trichlorobenzenethiolate (117 mg). UV λ_{max} (log ϵ_M): 384 (4.41), 468 (4.27), 586 (3.32), 642 (3.46) nm.

X-ray Experimental Section

A systematic search in reciprocal space using a Philips PW1100/6 automatic diffractometer showed that both crystalline forms **1a** and **1b** belong to the triclinic system. Their unit cells and standard deviations were obtained and refined at room temperature with Cu Kα- radiation (λ = 1.5418 Å) by using 25 carefully selected reflections and the standard Philips software. Final results and experimental data collection parameters are given in Table I. Three standard reflections measured every hour during the entire data collection period showed no significant trends. For all computations, the Enraf-Nonius S.D.P. package[6] was used on a PDP 11/60 computer, with the exception of a local data reduction program. The raw step-scan data were converted to intensities by using the Lehmann-Larson method[7] and then corrected for Lorentz, polarization, and absorption factors, the latter computed by the numerical integration method of Busing and Levy.[8]

Both structures were solved by using the heavy-atom method. After refinement of the heavy atoms, a difference Fourier map revealed maxima of residual electronic density close to the positions expected for hydrogen atoms; they are introduced in structure factor calculations by their computed coordinates (C–H = 0.95 Å) and isotropic temperature factors of 8 Å^2 for **1a** and 9 Å^2 for **1b** but not refined. Full least-squares refinements converged to conventional *R* factors given in Table I. Final difference maps revealed no significant maxima.

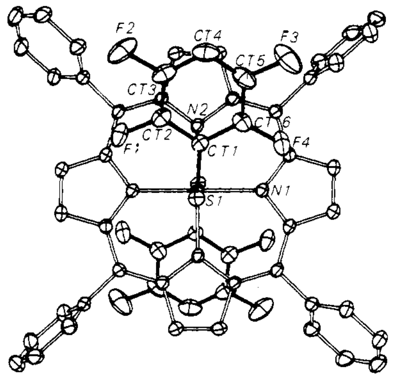

Figure 1. ORTEP plot of **1a**, bis(mercapto)cobalt(III) porphyrin. Ellipsoids are scaled to enclose 40% of the electronic density. Hydrogen atoms are omitted.

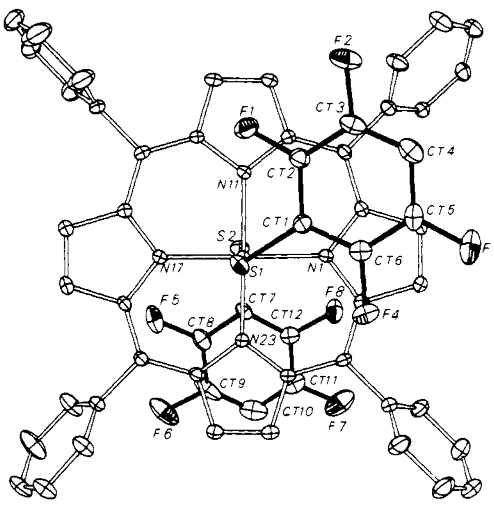

Figure 2. ORTEP plot of **1b**, bis(mercapto)cobalt(III) porphyrin. Ellipsoids are scaled to enclose 40% of the electronic density. Hydrogen atoms are omitted.

Table II gives the atomic positional parameters for **1a** and Table III for **1b** (non-hydrogen atoms).

Results and Discussion

Table IV gives selected bond distances and angles found in **1a** and **1b**. The asymmetric unit of **1a** contains two half-independent $[Co(SC_6HF_4)_2(TPP)]^-$ anions located on a crystallographic inversion center together with one $[Na\subset 222]$ cation and one C_6H_5Cl solvent molecule. Figure 1 shows one of these centrosymmetric $[Co(SC_6HF_4)_2(TPP)]^-$ anions.

No crystallographic symmetry is imposed on the $[Co(SC_6HF_4)_2(TPP)]^-$ ions in **1b**. The asymmetric unit of these crystals contains one such anion, one $[Na\subset 222]$ cation, and half of a disordered C_6H_5Cl solvent molecule (lying on an inversion center). Figure 2 shows the geometry of the $[Co(SC_6HF_4)_2(TPP)]^-$ anion present in **1b**.

As shown by Figures 1 and 2 the structures of these porphyrin anions differ essentially by the relative orientations of the 2,3,5,6-tetrafluorobenzenethiolato axial ligands, a result which is clearly due only to the molecular packing.

In **1a**, the cobalt and the porphyrinato nitrogens of the octahedral coordination unit form a necessarily square planar equatorial entity with $(Co1–N_p)_{av}$ = 1.978 (4) Å, $(Co2–N_p)_{av}$ = 1.976 (4) Å, $(N_p–Co1–N_p)_{av}$ = 89.9 (1)°, and $(N_p–Co2–N_p)_{av}$ = 89.8 (1)°. These distances and angles are identical with those present in the six-coordinate cobalt(III) derivative $[Co^{III}(Pip)_2(TPP)]^+$,[9] in which the metal lies also on a crystallographic inversion center. In contrast, in **1b**, due to a small ruffling[10] of the porphyrin core

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Table II. Positional Parameters and Their Estimated Standard Deviations

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
Co1	0.000	0.000	0.000	2.81 (3)	C8	0.2717 (5)	0.4861 (3)	0.6557 (6)	3.9 (2)
N1	0.0523 (4)	−0.0615 (2)	0.0877 (4)	3.3 (1)	C81	0.3897 (7)	0.4787 (4)	0.7307 (8)	5.7 (2)
C11	0.1370 (5)	−0.1016 (3)	0.0770 (6)	3.4 (2)	C82	0.4707 (9)	0.4955 (5)	0.708 (2)	11.7 (5)
C12	0.1483 (6)	−0.1406 (3)	0.1528 (6)	3.8 (2)	C83	0.592 (1)	0.4910 (6)	0.788 (2)	20.5 (8)
C13	0.0729 (6)	−0.1238 (3)	0.2081 (6)	4.0 (2)	C84	0.5898 (9)	0.4682 (6)	0.861 (2)	15.5 (5)
C14	0.0138 (5)	−0.0750 (3)	0.1683 (5)	3.3 (1)	C85	0.526 (1)	0.4494 (8)	0.899 (1)	15.7 (6)
N2	−0.1123 (4)	0.0229 (2)	0.0784 (4)	3.3 (1)	C86	0.4209 (9)	0.4570 (7)	0.826 (1)	10.9 (4)
C21	−0.1256 (5)	−0.0003 (3)	0.1654 (5)	3.7 (2)	S2	−0.0359 (2)	0.45459 (7)	0.6279 (2)	4.31 (4)
C22	−0.2109 (6)	0.0314 (3)	0.2067 (6)	4.7 (2)	CT7	−0.0441 (6)	0.5034 (3)	0.7519 (6)	3.8 (2)
C23	−0.2483 (6)	0.0727 (3)	0.1457 (6)	4.5 (2)	CT8	0.0460 (6)	0.5148 (3)	0.8580 (6)	4.3 (2)
C35	−0.1869 (5)	0.0673 (3)	0.0670 (6)	3.4 (2)	CT9	0.0372 (6)	0.5502 (3)	0.9558 (6)	4.3 (2)
C5	−0.0687 (6)	−0.0464 (3)	0.2069 (6)	3.9 (2)	CT10	−0.0577 (7)	0.5788 (4)	0.9595 (6)	5.2 (2)
C51	−0.0987 (6)	−0.0649 (3)	0.2999 (6)	4.1 (2)	CT11	−0.1479 (6)	0.5687 (3)	0.8578 (7)	4.9 (2)
C52	−0.0247 (7)	−0.0633 (3)	0.4159 (6)	5.1 (2)	CT12	−0.1411 (6)	0.5329 (3)	0.7592 (6)	4.3 (2)
C53	−0.0576 (8)	−0.0749 (4)	0.5018 (7)	6.4 (2)	F5	0.1443 (4)	0.4874 (2)	0.8644 (4)	5.8 (1)
C54	−0.1637 (9)	−0.0880 (4)	0.4756 (7)	8.3 (3)	F6	0.1285 (4)	0.5601 (2)	1.0563 (4)	7.2 (2)
C55	−0.2395 (7)	−0.0910 (4)	0.3619 (8)	6.9 (2)	F7	−0.2439 (4)	0.5971 (3)	0.8568 (5)	8.2 (2)
C56	−0.2078 (6)	−0.0789 (4)	0.2729 (7)	5.6 (2)	F8	−0.2320 (4)	0.5250 (2)	0.6641 (4)	6.5 (1)
C6	0.2002 (5)	−0.1043 (3)	0.0057 (5)	3.3 (2)	Na	0.6006 (3)	0.2558 (1)	0.5180 (3)	5.22 (8)
C61	0.2888 (6)	−0.1491 (3)	0.0064 (6)	4.1 (2)	N1C	−0.4460 (7)	−0.1809 (3)	0.5036 (8)	7.7 (3)
C62	0.3996 (7)	−0.1385 (4)	0.0581 (8)	6.0 (2)	C2C	−0.503 (1)	−0.1264 (4)	0.511 (1)	9.9 (4)
C63	0.4814 (7)	−0.1773 (4)	0.0525 (9)	6.6 (3)	C3C	−0.616 (1)	−0.1260 (4)	0.441 (1)	11.6 (5)
C64	0.4543 (7)	−0.2308 (4)	−0.0083 (7)	6.0 (2)	O4C	−0.6767 (7)	−0.1608 (3)	0.4646 (9)	11.4 (3)
C65	0.3502 (7)	−0.2426 (3)	−0.0583 (8)	5.3 (2)	C5C	−0.729 (1)	−0.1380 (5)	0.558 (1)	12.8 (5)
C66	0.2674 (7)	−0.2033 (3)	−0.0513 (7)	5.0 (2)	C6C	−0.788 (1)	−0.1780 (6)	0.569 (1)	13.7 (5)
S1	0.1099 (2)	0.05861 (7)	0.1679 (2)	3.92 (4)	O7C	−0.7291 (6)	−0.2241 (4)	0.5928 (7)	10.4 (3)
CT1	0.2462 (5)	0.0432 (3)	0.1748 (6)	3.8 (2)	C8C	−0.7790 (9)	−0.2680 (6)	0.617 (1)	11.2 (4)
CT2	0.3182 (6)	0.0100 (3)	0.2479 (7)	5.0 (2)	C9C	−0.8250 (9)	−0.3092 (6)	0.507 (1)	10.4 (4)
CT3	0.4242 (8)	0.0005 (4)	0.2565 (9)	7.0 (3)	N10C	−0.7559 (7)	−0.3351 (3)	0.4442 (6)	7.6 (2)
CT4	0.4671 (7)	0.0185 (4)	0.187 (1)	7.6 (3)	C11C	−0.691 (1)	−0.3799 (5)	0.490 (1)	12.7 (4)
CT5	0.4021 (7)	0.0496 (5)	0.1110 (8)	7.5 (3)	C12C	−0.583 (1)	−0.0841 (5)	0.502 (1)	12.1 (5)
CT6	0.2898 (7)	0.0639 (3)	0.1048 (7)	5.3 (2)	O13C	−0.5297 (7)	−0.3361 (3)	0.5674 (8)	11.4 (3)
F1	0.2816 (4)	−0.0117 (2)	0.3181 (4)	7.1 (1)	C14C	−0.4538 (9)	−0.3340 (5)	0.683 (1)	8.9 (3)
F2	0.4892 (5)	−0.0328 (3)	0.3294 (7)	11.1 (2)	C15C	−0.412 (1)	−0.2815 (5)	0.7350 (9)	9.0 (4)
F3	0.4355 (4)	0.0725 (3)	0.0420 (6)	10.7 (2)	O16C	−0.4070 (8)	−0.2531 (3)	0.6601 (7)	11.7 (3)
F4	0.2295 (4)	0.0990 (2)	0.0356 (4)	6.5 (1)	C17C	−0.371 (1)	−0.1997 (6)	0.701 (1)	11.1 (5)
Co2	0.000	0.500	0.500	2.77 (3)	C18C	−0.352 (1)	−0.1813 (5)	0.614 (1)	10.8 (4)
N3	−0.1051 (4)	0.4533 (2)	0.3660 (4)	3.0 (1)	C19C	−0.416 (1)	−0.1988 (5)	0.398 (1)	9.6 (4)
C31	−0.2146 (5)	0.4654 (3)	0.3124 (6)	3.4 (2)	C20C	−0.4098 (8)	−0.2583 (5)	0.358 (1)	9.2 (4)
C32	−0.2626 (6)	0.4203 (3)	0.220, (7)	4.4 (2)	O21C	−0.5099 (5)	−0.2846 (3)	0.3308 (5)	7.3 (2)
C33	−0.1841 (6)	0.3810 (3)	0.2165 (6)	4.0 (2)	C22C	−0.575 (1)	−0.2877 (7)	0.2150 (9)	11.2 (4)
C34	−0.0846 (6)	0.4004 (3)	0.3046 (5)	3.4 (2)	C23C	−0.6788 (9)	−0.3107 (5)	0.1914 (9)	8.5 (3)
N4	0.1172 (4)	0.4412 (2)	0.4924 (4)	3.2 (1)	O24C	−0.7334 (5)	−0.2801 (3)	0.2695 (5)	7.0 (2)
C41	0.1110 (6)	0.3907 (3)	0.4164 (6)	3.8 (2)	C25C	−0.8330 (8)	−0.3017 (5)	0.2586 (8)	7.4 (3)
C42	0.2143 (6)	0.3612 (3)	0.4421 (7)	4.4 (2)	C26C	−0.8141 (8)	−0.3502 (4)	0.3161 (9)	7.7 (3)
C43	0.2866 (6)	0.3927 (3)	0.5341 (7)	4.5 (2)	C1[a]	0.7763 (5)	0.7939 (2)	0.0622 (5)	16.2 (2)
C44	0.2258 (5)	0.4426 (3)	0.5641 (6)	3.6 (2)	CS1[a]	0.8099 (9)	0.7498 (5)	0.161 (1)	8.5 (3)
C7	0.0137 (6)	0.3707 (3)	0.3285 (6)	3.5 (2)	CS2[a]	0.771 (1)	0.7074 (7)	0.109 (1)	12.5 (5)
C71	0.0213 (6)	0.3133 (3)	0.2566 (6)	3.5 (2)	CS3[a]	0.746 (3)	0.661 (1)	0.107 (3)	26 (1)
C72	0.0106 (7)	0.3035 (3)	0.1394 (7)	5.2 (2)	CS4[a]	0.817 (1)	0.6558 (7)	0.231 (1)	12.7 (5)
C73	0.0196 (8)	0.2511 (4)	0.0712 (8)	5.9 (2)	CS5[a]	0.865 (1)	0.6891 (6)	0.316 (1)	10.0 (3)
C74	0.0405 (7)	0.2072 (3)	0.1261 (8)	5.6 (2)	CS6[a]	0.870 (2)	0.7508 (9)	0.306 (2)	16.8 (7)
C75	0.0504 (7)	0.2154 (3)	0.2445 (8)	5.1 (2)					
C76	0.0408 (7)	0.2674 (3)	0.3093 (7)	4.7 (2)					

[a] Atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(4/3)[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$.

(vide infra), a slight reduction of the $(\text{Co–Np})_{\text{av}}$ bond distance is visible; the average bond distance is now 1.973 (4) Å. In **1a**, the axial ligands are arranged centrosymmetrically; the opposite necessarily linear Co–S bonds (in both anions present in **1a**) eclipse two opposite Co–Np bonds. The Co–S bond distances corresponding to both centrosymmetric anions are respectively 2.346 (3) and 2.330 (3) Å. Moreover, the Co–S bonds are tipped respectively by 5.79° and 4.74°.

In **1b**, the Co–S1–C(C_6HF_4) group has almost a staggered orientation with respect to two adjacent Co–Np bonds and the N1–Co–S1/Co–S1–CT1 dihedral angle is equal to 32.6°. The Co–S2–C(C_6HF_4) unit lies in an eclipsed orientation with respect to the Co–Np_{23} bond. The Co–S1 and Co–S2 bond distances of 2.346 (3) and 2.351 (3) Å are within experimental error identical with those found in **1a**. They are also tipped 5.79° and 4.74°, respectively, from the normal to the porphyrin plane.

So far, no mercaptocobalt porphyrin derivatives were structurally characterized. A comparison with non-porphyrin mercaptocobalt(III) complexes shows that the Co–S bond distances present in **1a** and **1b** are rather long: Co^{III}–S = 2.275 (2) Å in K[Co(D-pen) (L-pen)]·$2H_2O$[11] and 2.272 (2) Å in [Co(*S*-Me-L-cysteinate)$_2$]ClO_4·H_2O.[12] Moreover, they lie at the long end of the range (2.22–2.34 Å) known for several nonporphyrin mercaptocobalt(II) complexes.[13,14] This equation is similar to that occurring with mercaptoiron(II) and -iron(III) porphyrins where

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Table III. Positional Parameters and Their Estimated Standard Deviations

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
Co	0.26535 (4)	0.26187 (5)	0.13622 (5)	2.19 (2	CT1	0.4053 (3)	0.1149 (3)	0.0826 (3)	3.1 (1)
N1	0.3271 (2)	0.2754 (2)	0.0363 (2)	2.53 (8)	CT2	0.4801 (3)	0.1366 (4)	0.1536 (4)	3.7 (1)
C2	0.3002 (3)	0.2430 (3)	−0.0623 (3)	2.8 (1)	CT3	0.5581 (4)	0.1372 (4)	0.1274 (4)	4.6 (1)
C3	0.3668 (3)	0.i2561 (3)	−0.1120 (3)	3.1 (1)	CT4	0.5704 (4)	0.1188 (4)	0.0355 (5)	5.1 (2)
C4	0.4335 (3)	0.2990 (3)	−0.0442 (3)	3.4 (1)	CT5	0.4975 (4)	0.0961 (4)	−0.0360 (4)	4.5 (1)
C5	0.4086 (3)	0.3127 (3)	0.0474 (3)	2.9 (1)	CT6	0.4194 (4)	0.0923 (3)	−0.0118 (4)	3.7 (1)
C6	0.4625 (3)	0.3554 (3)	0.1369 (3)	3.1 (1)	F1	0.4752 (2)	0.1557 (2)	0.2466 (2)	5.27 (9)
C7	0.4390 (3)	0.3581 (3)	0.2235 (3)	2.9 (1)	F2	0.6277 (2)	0.1583 (3)	0.2013 (3)	6.7 (1)
C8	0.4927 (3)	0.4000 (4)	0.3161 (4)	3.7 (1)	F3	0.5053 (3)	0.0747 (3)	−0.1286 (2)	6.9 (1)
C9	0.4553 (3)	0.3800 (4)	0.3828 (4)	3.9 (1)	F4	0.3514 (2)	0.0656 (2)	−0.0846 (2)	5.01 (8)
C10	0.3766 (3)	0.3281 (3)	0.3328 (3)	2.9 (1)	S2	0.22211 (9)	0.40600 (8)	0.1694 (1)	3.76 (3)
N11	0.3670 (2)	0.3172 (3)	0.2348 (3)	2.79 (9)	CT7	0.1286 (3)	0.4029 (3)	0.0881 (4)	3.5 (1)
C12	0.3222 (3)	0.2956 (3)	0.3778 (3)	3.3 (1)	CT8	0.0475 (4)	0.3978 (4)	0.1099 (5)	4.7 (1)
C13	0.2403 (3)	0.2544 (3)	0.3306 (3)	3.2 (1)	CT9	−0.0265 (4)	0.3919 (4)	0.0398 (6)	6.7 (2)
C14	0.1801 (4)	0.2253 (4)	0.3791 (4)	4.2 (1)	CT10	−0.0210 (5)	0.3917 (4)	−0.0502 (6)	6.7 (2)
C15	0.1079 (3)	0.1990 (4)	0.3146 (4)	4.2 (1)	CT11	0.0570 (5)	0.3995 (4)	−0.0695 (5)	5.7 (2)
C16	0.1236 (3)	0.2089 (3)	0.2249 (3)	2.9 (1)	CT12	0.1292 (4)	0.4055 (3)	−0.0037 (4)	4.0 (1)
N17	0.2056 (2)	0.2425 (3)	0.2368 (3)	2.68 (9)	F5	0.0399 (2)	0.3962 (3)	0.1986 (3)	6.8 (1)
C18	0.0641 (3)	0.1873 (3)	0.1413 (3)	2.6 (1)	F6	−0.1016 (3)	0.3855 (3)	0.0708 (4)	9.9 (2)
C19	0.0846 (3)	0.1903 (3)	0.0548 (3)	2.5 (1)	F7	0.0628 (4)	0.4052 (3)	−0.1583 (3)	9.4 (1)
C20	0.0232 (3)	0.1651 (3)	−0.0351 (3)	3.3 (1)	F8	0.2027 (2)	0.4142 (2)	−0.0328 (2)	5.90 (9)
C21	0.0664 (3)	0.1681 (3)	−0.1043 (4)	3.5 (1)	N1C	0.2545 (4)	0.9213 (4)	0.2455 (4)	6.1 (2)
C22	0.1539 (3)	0.1963 (3)	−0.0586 (3)	2.6 (1)	C2C	0.2743 (6)	0.8769 (6)	0.1483 (5)	8.6 (3)
N23	0.1625 (2)	0.2119 (2)	0.0392 (2)	2.29 (8)	C3C	0.2344 (7)	0.7837 (6)	0.1083 (5)	8.9 (3)
C24	0.2175 (3)	0.2069 (3)	−0.1084 (3)	2.9 (1)	O4C	0.2628 (4)	0.7302 (4)	0.1665 (4)	8.1 (2)
C25	0.5480 (3)	0.3939 (3)	0.1353 (3)	3.1 (1)	C5C	0.3302 (8)	0.6868 (9)	0.1457 (7)	14.1 (4)
C26	0.5571 (3)	0.4631 (3)	0.0980 (3)	3.1 (1)	C6C	0.3573 (6)	0.6284 (6)	0.2028 (8)	10.1 (3)
C27	0.6362 (3)	0.4954 (3)	0.0929 (4)	3.7 (1)	O7C	0.3600 (4)	0.6716 (3)	0.2987 (4)	8.2 (2)
C28	0.7077 (4)	0.4619 (4)	0.1260 (4)	4.4 (1)	C8C	0.3840 (7)	0.6233 (7)	0.3628 (9)	18.5 (3)
C29	0.7017 (4)	0.3936 (4)	0.1648 (5)	4.9 (2)	C9C	0.3466 (9)	0.6184 (7)	0.4233 (8)	14.4 (4)
C30	0.6220 (4)	0.3604 (3)	0.1690 (4)	4.2 (1)	N10C	0.2734 (5)	0.6702 (4)	0.4506 (5)	8.4 (2)
C31	0.3493 (4)	0.3041 (4)	0.4818 (3)	4.0 (1)	C11C	0.2917 (8)	0.7232 (7)	0.5536 (6)	10.7 (3)
C32	0.3938 (5)	0.2429 (5)	0.5087 (4)	6.7 (2)	C12C	0.2541 (8)	0.8095 (7)	0.5761 (6)	10.1 (3)
C33	0.4188 (6)	0.2525 (5)	0.6076 (5)	8.6 (2)	O13C	0.2809 (4)	0.8613 (4)	0.5233 (3)	8.2 (2)
C34	0.4003 (5)	0.3236 (5)	0.6754 (4)	7.8 (2)	C14C	0.3575 (6)	0.9171 (6)	0.5659 (5)	8.3 (2)
C35	0.3571 (5)	0.3841 (6)	0.6505 (4)	8.0 (2)	C15C	0.3671 (6)	0.9732 (5)	0.5041 (5)	7.3 (2)
C36	0.3301 (5)	0.3783 (5)	0.5528 (4)	6.3 (2)	O16C	0.3782 (3)	0.9186 (3)	0.4134	6.9 (1)
C37	−0.0254 (3)	0.1563 (3)	0.1425 (3)	2.9 (1)	C17C	0.3948 (6)	0.9640 (6)	0.3482 (6)	9.2 (2)
C38	−0.0548 (4)	0.0697 (4)	0.1017 (4)	4.3 (1)	C18C	0.3200 (6)	0.9944 (5)	0.3014 (6)	8.6 (2)
C39	−0.1373 (4)	0.0414 (4)	0.0987 (5)	5.3 (2)	C19C	0.1692 (6)	0.9562 (6)	0.2421 (6)	8.7 (3)
C40	−0.1916 (4)	0.0994 (4)	0.1387 (5)	5.2 (2)	C20C	0.1297 (5)	0.9517 (5)	0.3224 (6)	7.8 (2)
C41	−0.1638 (4)	0.1850 (4)	0.1822 (6)	7.2 (2)	O21C	0.1194 (4)	0.8661 (4)	0.317. (5)	11.6 (2)
C42	−0.0812 (4)	0.2145 (4)	0.1828 (5)	5.6 (2)	C22C	0.0650 (5)	0.8403 (6)	0.3561 (7)	9.6 (3)
C43	0.1980 (3)	0.1802 (3)	−0.2168 (3)	3.3 (1)	C23C	0.0551 (5)	0.7491 (6)	0.3490 (6)	8.1 (3)
C44	0.1917 (4)	0.2423 (4)	−0.2620 (4)	4.2 (1)	O24C	0.1302 (4)	0.7091 (4)	0.3402 (4)	9.4 (2)
C45	0.1733 (5)	0.2175 (5)	−0.3633 (4)	5.6 (2)	C25C	0.1351 (7)	0.6242 (7)	0.3404 (8)	12.4 (3)
C46	0.1606 (5)	0.1300 (5)	−0.4159 (4)	5.8 (2)	C26C	0.1897 (8)	0.6178 (6)	0.4255 (9)	12.8 (4)
C47	0.1683 (5)	0.0681 (4)	−0.3728 (4)	5.6 (2)	Na	0.2617 (2)	0.7899 (2)	0.3430 (2)	5.05 (6)
C48	0.1855 (5)	0.0928 (4)	−0.2717 (4)	4.9 (2)	CS1[a]	0.9902 (9)	0.5535 (9)	0.569 (1)	5.9 (3)
S1	0.30472 (8)	0.11763 (8)	0.11425 (9)	3.52 (3)	CS2[a]	0.910 (1)	0.494 (1)	0.380 (1)	9.4 (5)
					CS3[a]	1.068 (2)	0.438 (2)	0.501 (2)	11.3 (7)
					C1S[a]	0.8874 (7)	0.5414 (7)	0.4146 (8)	6.9 (2)

[a] Atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(4/3)[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$.

the Fe–S distances lie also at the long end of the range known for non-porphyrin mercaptoiron(II) and -iron(III) complexes.[15-18]

The electron-withdrawing fluorosubstituents of the thiolato ligand could be partly responsible for the long Co–S bonds, their effect must however be quite small. In $[Fe(SC_6H_5)_2(TPP)]^-$[19] and $[Fe(SC_6F_4)_2(TPP)]^-$,[20] the Fe–S bond distances are slightly shorter in the tetrafluorobenzenethiolato complex (2.312 (1) Å at 20 °C) than in the benzenethiolato compound (2.346 (4) Å at 20 °C and 2.336 (2) Å at 115 K).

The 24-atom cores of the two independent centrosymmetric porphyrins present in **1a** are almost identical. Whereas the Co2 core is planar within experimental error, the Co1 core departs slightly from planarity (Figure 3). As usually, the pyrrole rings

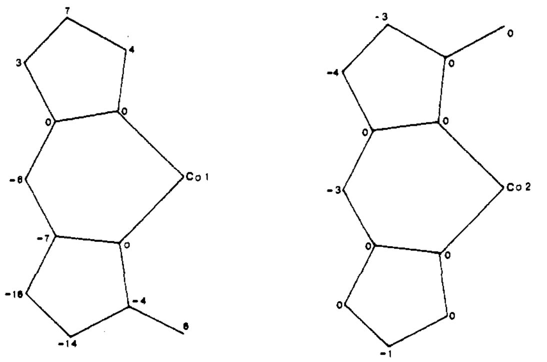

Figure 3. Stick model for the two **1a** half-porphyrin cores. Numbers indicate in 0.01 Å the deviation of each atom from the half-core mean plane.

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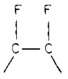
Table IV. Bond Distances (Å) and Bond Angles (deg) with Their Estimated Standard Deviations

1a		**1b**	
Co1–S1	2.346 (3)	Co–S1	2.346 (3)
Co2–S2	2.330 (3)	Co–S2	2.351 (3)
Co1–N1	1.987 (4)	Co–N1	1.967 (4)
Co1–N2	1.970 (4)	Co–N11	1.976 (4)
Co2–N3	1.971 (4)	Co–N17	1.988 (4)
Co2–N4	1.981 (4)	Co–N23	1.963 (4)
	Pyrrole Rings		
N–C_α	1.382 (3)	1.372 (3)	
C_α–C_β	1.431 (3)	1.441 (3)	
C_β–$C_{\beta'}$	1.349 (4)	1.340 (4)	
C_α–C_m	1.381 (3)	1.390 (3)	
	Phenyl Rings		
C_m–C_p	1.502 (4)	1.498 (4)	
C–C	1.366 (4)	1.373 (3)	
	Thiolate Phenyl Rings		
S–C	1.738 (4)	1.744 (4)	
C–C	1.371 (3)	1.374 (3)	
C–F	1.348 (4)	1.351 (4)	
	Cryptates		
N–C	1.435 (5)	1.483 (5)	
C–O	1.403 (5)	1.376 (5)	
C–C	1.423 (5)	1.437 (5)	
Na–N	2.846 (6), 2.880 (5)	2.835 (5), 2.891 (5)	
Na–O	2.402 (5)–2.687 (6)	2.440 (4)–2.635 (5)	
S1–Co1–N1	89.0 (1)	S1–Co–N1	92.3 (1)
S1–Co1–N1′	90.9 (1)	S1–Co–N17	84.9 (1)
S1–Co1–N2	84.1 (1)	S1–Co–N11	94.3 (1)
S1–Co1–N2′	95.8 (1)	S1–Co–N23	88.1 (1)
S2–Co2–N3	87.5 (1)	S2–Co–N1	92.2 (1)
S2–Co2–N3′	92.4 (1)	S2–Co–N17	90.6 (1)
S2–Co2–N4	85.9 (1)	S2–Co–N11	84.9 (1)
S2–Co2–N4′	94.1 (1)	S2–Co–N23	92.7 (1)
N1–Co1–N2	89.6 (1)	N1–Co–N11	89.0 (1)
		N1–Co–N17	177.1 (1)
N1–Co1–N2′	90.3 (1)	N1–Co–N23	91.0 (1)
N3–Co2–N4	89.2 (1)	N11–Co–N17	90.7 (1)
		N11–Co–N17	90.7 (1)
N3–Co2–N4′	90.7 (1)	N11–Co–N23	177.5 (1)
		N17–Co–N23	89.3 (1)
Co1–S1–CT1	108. (1)		
Co2–S2–CT7	107.5 (1)	Co–S1–CT1	106.3 (1)
		Co–S2–CT7	107.9 (1)
Co–N–C_α	127.5 (1)		127.2 (1)
	Pyrrole Rings		
C_α–N–$C_{\alpha'}$	104.9 (2)	105.3 (2)	
N–C_α–C_β	110.2 (1)	110.3 (1)	
C_α–C_β–$C_{\beta'}$	107.3 (1)	107.0 (1)	
N–C_α–C_m	125.6 (1)	126.0 (1)	
C_α–C_m–$C_{\alpha m}$	123.7 (2)	122.4 (2)	
C_α–C_m–C_p	118.7 (1)	118.1 (1)	
	Phenyl Rings		
C–C–C	120.0 (2)	120.0 (1)	
	Thiolate Rings		
S–C_α–C_β	122.7 (2)	122.9 (1)	
C_β–C_α–C_β	114.4 (3)	114.2 (2)	
C–CH–C	117.5 (3)	116.6 (2)	
	120.7 (6)–123.1 (4)	120.2 (3)–124.3 (3)	

are planar and their dihedral angles with the Co1 porphyrin mean plane are 1.9° and 4.1°.

In **1b**, the 24-atom core of the porphyrin anion is slightly ruffled[10] (Figure 4). The dihedral angles between the planes of the pyrrole rings and the 24-atom core mean plane being now +8.8°, -8.7°, +8.0°, and -7.7°. Using C_α and C_β to denote the respective α and β carbons in a pyrrole ring, C_m for methyne carbon and C_p for a phenyl carbon that is bonded to the core, average bond lengths for the chemically analogous types of bonds are respectively in **1a** and **1b**: N–C_α = 1.382 (3) and 1.372 (3) Å, C_α–C_β = 1.431 (3) and 1.441 (3) Å, C_β–C_β = 1.349 (4) and 1.340 (4) Å, C_α–C_m = 1.381 (3) and 1.390 (3) Å, C_m–C_p = 1.502 (4) and 1.498 (4) Å.

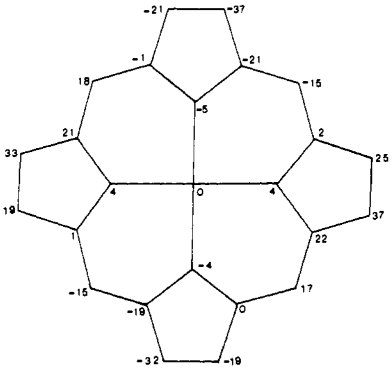


Figure 4. Stick model for the **1b** porphyrin core. Number indicate in 0.01 Å the deviation of each atom from the core mean plane.

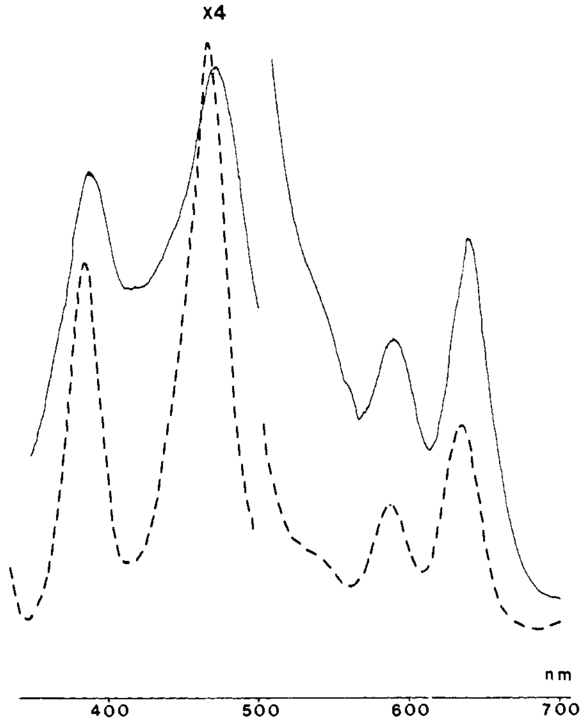


Figure 5. UV-visible spectrum at 25 °C of $[Co(SC_6HF_4)_2(TPP)][Na\subset 222]$ solid (full line) and in C_6H_5Cl (broken line).

The chemically analogous types of bond angles are respectively in **1a** and **1b**: Co–N–C_α = 127.5 (1)°, 127.2 (1)°, C_α–N–C_α = 104.9 (2)° and 105.3 (2)°, N–C_α–C_β = 120.2 (1)° and 110.3 (1)°, C_α–C_β–C_β = 107.3 (1)° and 107.0 (1)°, N–C_α–C_m = 125.6 (1)° and 126.0 (1)°, C_α–C_m–C_α = 123.7 (2)° and 122.4 (2)°, C_α–C_m–C_p = 118.7 (1)° and 118.1 (1)°.

The phenyl rings have normal geometries in both structures. Their dihedral angles with the porphyrin core mean plane are 60.7°, 73.0°, 68.5°, and 87.8° in **1a**, 57.4°, 82.4° 68.9°, and 66.6° in **1b**.

The mean value of the S–C(C_6HF_4) bond distance is 1.741 (4) Å and the average Co–S–C bond angle is 107.4 (1)°. The C_6HF_4 rings are planar within experimental error; the C–C–C bond angles are slightly affected by the different substituents (see Table I). In both complexes, the negative charge of the porphyrin anion is balanced by a $[Na\subset 222]$ cation. Table I gives some significant bond lengths within these ions. Their values do not differ from those found elsewhere.[21] The C_6H_5Cl solvent molecule in **1a** has

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[21] Moras, D.; Weiss, R. *Acta Crystallogr., Sect. B* **1973**, *B29, part 3*, 396–399.

a normal geometry. In **1b**, it lies on an inversion center; thus the chlorine atom is statistically disordered over six positions.

Both compounds **1** and **2** which are diamagnetic six-coordinate cobalt(III) porphyrins present a d-type hyperporphyrin electronic spectrum[22,23] (Figure 5) with split Soret bands lying close to 384 and 465 nm for which there is no precedent for in cobalt porphyrin systems.[1,24] These spectra also closely resemble the spectra of dimercaptoiron(III)[25] -ruthenium(III)[26] and -chromium(III)[27] porphyrin derivatives. d-Type hyperporphyrin spectral properties seem to be a characteristic feature of dimercapto metalloporphyrins. Moreover, these spectral properties of the dimercaptocobalt compounds are essentially identical with those of the species obtained by treatment of the native state of cobalt-substituted cytochrome $P450_{CAM}$ with dithiothreitol[1] (Figure 5) which are also very similar to those of the ferric counterpart.[28] Thus, the spectral properties of the dimercaptocobalt porphyrins that we have synthesized indicate that the treatment of Co $P450_{CAM}$ with dithiothreitol yields most probably a dimercaptocobalt(III) species and confirms indirectly what is now commonly accepted, that is, cysteinate axial ligation to the metal in the resting state of cytochrome P450.

Registry No. 1a, 91128-01-7; **1b**, 91128-02-8; **2**, 91128-04-0; $[Co^{III}(Cl)(TPP)]$, 60166-10-1; $[Co^{II}(SC_6HF_4)(TPP)][Na\subset 222]$, 91157-01-6; cryptand 222, 23978-09-8; sodium 2,3,5,6-tetrafluorobenzenethiolate, 91156-99-9; sodium 2,4,5-trichlorobenzenethiolate, 91157-00-5.

Supplementary Material Available: Listings of hydrogen atom parameters for **1a** (Table V) and **1b** (Table VI), thermal parameters for non-hydrogen atoms of **1a** (Table VII) and **1b** (Table VIII), and observed and calculated structure factors (× 10) for all observed reflections for **1a** (Table IX) and **1b** (Table X) (71 pages). Ordering information is given on any current masthead page.

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Removal of Glycine from Cu(II) upon Peptide Proton Ionization in a Mixed-Ligand Cu(II)–Peptide–Amino Acid Chelate. A Possible Model for Substrate Removal at Metalloenzyme Centers

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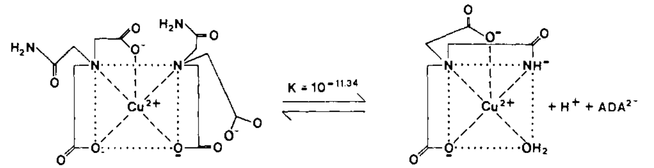
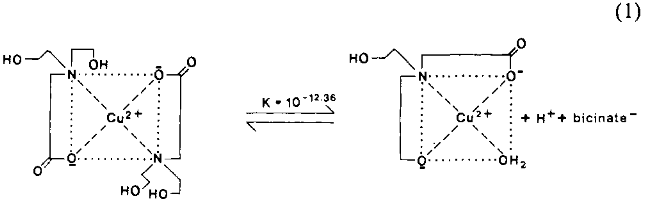
Abstract: Potentiometric, visible, and electron spin resonance studies indicate that the mixed-ligand metal complex, (glycylglycine-*N*,*N*-diacetato)(glycinato)copper(II), $[Cu(DGDA)gly^{2-}]$ undergoes loss of an amino acidate ligand upon peptide proton ionization, $[Cu(DGDA)gly^{2-}] \rightleftarrows [Cu(H_{-1}DGDA)^{2-}] + gly^- + H^+$, with a constant of $10^{-11.68\pm0.02}$. The possible importance of this reaction to substrate release at metalloenzyme centers is discussed.

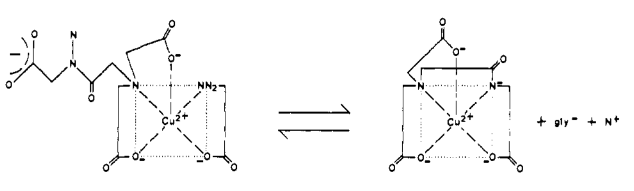
Previously, we have described amino acidate dechelation upon amide deprotonation[1] in the bis[*N*-acetamidoiminodiacetato]-copper(II) chelate (eq 1) and upon hydroxy group ionization[2] in the bis(*N*,*N*-bis(2-hydroxyethyl)glycinato)copper(II) chelate. In a continuing study of dechelation reactions in metal complexes, the mixed-ligand chelate (*N*,*N*-bis(carboxymethyl)glycylglycinato)(glycinato)copper(II) (I) was found to undergo loss of the glycinate ion upon peptide proton ionization (eq 3). The discovery of this reaction completes our initial goal of showing that (when ionized) the three strongest σ-donor groups present at the active sites of metalloenzymes, i.e., amide groups (asparagine, glutamine), alcohol groups (serine, threonine), and peptide groups, are capable of initiating dechelation reactions.



(1)



(2)



II

(3)

Experimental Section

Reagents. Baker Analyzed reagent grade $Cu(NO_3)_2 \cdot 3H_2O$ was used for all metal solutions, which were standardized via standard ion-exchange techniques. Aliquots of the metal ion solution were passed through Dowex 50W-X8 strongly acidic cation-exchange resin, and the

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