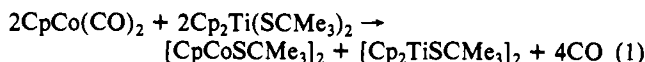
parameters are given in Tables I-III, respectively. The Co_2S_2 ring forms a shallow butterfly-type ring with a metal distance of 2.467 ± 1 Å, consistent with the presence of a metal-metal bond[11] and with the diamagnetism observed in the NMR spectrum.

The reaction between $CpCo(CO)_2$ and $Cp_2Ti(SCMe_3)_2$ in room-temperature hexanes does not proceed without irradiation. The reaction with $Cp_2Ti(SCHMe_2)_2$ gave a green crude product, the NMR spectrum of which was consistent with the presence of $[CpCoSCHMe_2]_2$, but pure product could not be isolated. Starting $Cp_2Ti(SCH_2Ph)_2$ was recovered from the reaction of this complex with $Cp_2Co(CO)_2$.

Discussion

The structure of $[CpCoSCMe_3]_2$ is the same as $[CpRhSPh]_2$;[12] however, it is interesting that the latter is static on the NMR time scale whereas the former is stereochemically nonrigid. Also of interest is the production of an additional isomer (possibly the equatorial-equatorial) in the preparation of the rhodium complex.[12] No evidence for the presence of any other isomers of the cobalt dimer was detected.

The routes to Cp-metal thiolate complexes have recently been discussed;[13] however, the preparation of $[CpCoSCMe_3]_2$ is quite novel. The irradiation of $CpCo(CO)_2$ in the presence of $Cp_2Ti(SCMe_3)_2$ was intended to produce the thiolato-bridged mixed-metal dimer $Cp_2Ti(\mu\text{-}SCMe_3)_2CoCp$, but instead a redox reaction occurred to give two homometal dimers: $[Cp_2TiSCMe_3]_2$ and $[CpCoSCMe_3]_2$ (eq 1). It is of interest that $[CpCoSCMe_3]_2$



$$2CpCo(CO)_2 + 2Cp_2Ti(SCMe_3)_2 \rightarrow [CpCoSCMe_3]_2 + [Cp_2TiSCMe_3]_2 + 4CO \quad (1)$$

could not be isolated from reaction of $CpCo(CO)_2$ with $S_2(CMe_3)_2$,[11a] the route that reportedly gave the methyl and phenyl analogues.[5]

Experimental Section

The general preparative methods and spectroscopic characterization techniques have been described.[14] The complex $CpCo(CO)_2$ (Strem) was used as received, and $Cp_2Ti(SCMe_3)_2$ was prepared from Cp_2TiCl_2 and $LiSCMe_3$.[15]

Bis(cyclopentadienyl)bis(μ-2-methylpropanethiolato)dicobalt(II), $[CpCoSCMe_3]_2$. A solution of $CpCo(CO)_2$ (0.30 g, 1.67 mmol) and $Cp_2Ti(SCMe_3)_2$ (0.59 g, 1.65 mmol) in hexanes (70 mL) was irradiated by using a mercury-vapor lamp (Hanovia, 100 W) and apparatus[16] previously described. The solution was slowly and continuously purged with N_2. The red solution became dark green, and a red precipitate formed on the walls of the apparatus. The progress of the reaction was monitored by following the decrease in intensity of the ν(CO) bands of $CpCo(CO)_2$ in infrared spectra taken at intervals. After 30 h only a trace of $CpCo(CO)_2$ was detected and the irradiation was terminated. The green supernatant was decanted under N_2 and saved. The red precipitate was washed with hexanes (3 × 20 mL), and the washings were added to the green supernatant. The red precipitate was pumped overnight and then scraped from the flask to give $[Cp_2TiSCMe_3]_2$ (0.39 g, 88%, mp 198-200 °C dec). Anal. Calcd for $C_{28}H_{38}S_2Ti_2$: C, 62.92; H, 7.16; S, 12.00. Found: C, 62.90; H, 7.18; S, 11.99.

The combined supernatant and washings were filtered under N_2, and the filtrate was reduced in volume under vacuum to about 10 mL. Cooling the solution under N_2 to -78 °C (dry ice) gave dark green microcrystals of $[CpCoSCMe_3]_2$ (0.21 g, 60%, mp 114-115 °C). ^1H NMR (toluene-d_8): δ 4.76 (s, 5, C_5H_5), 1.70-0.89 (b, 9, $C(CH_3)_3$). Mass spectrum, m/z (relative intensity, assignment): 425 (29, $M^+ - H$), 369 (14, $M^+ - C_4H_9$), 312 (238, $M^+ - C_8H_{18}$) 280 (26, $M^+ - C_8H_8S$), 248 (20, $C_8H_{18}S_2$). Anal. Calcd for $C_{18}H_{28}Co_2S_2$: C, 50.69; H, 6.23; S, 15.04. Found: C, 50.73; H, 6.74; S, 14.94.

X-ray Structure Determination. Table I contains the crystal parameters for $[CpCoSCMe_3]_2$. A large, approximately cube-shaped dark green crystal obtained by recrystallization from hexanes at -16 °C was glued with epoxy to the inside of a thin-walled glass capillary and sealed under N_2. A total of 4529 independent reflections having 2θ(Mo K$\bar{\alpha}$) < 55.0 ° (the equivalent of 1.0 limiting Cu K$\bar{\alpha}$ sphere) were collected on a computer-controlled Nicolet autodiffractometer using full (0.90° wide) ω scans and graphite-monochromated Mo K$\bar{\alpha}$ radiation. The structure was solved by using direct methods techniques with the Nicolet SHELXTL software package as modified at Crystalytics Co. The resulting structural parameters have been refined to convergence [R_1(unweighted, based on F) = 0.037 for 3160 independent reflections having 2θ(Mo K$\bar{\alpha}$) < 55.0° and $I > 3\sigma(I)$] by using counter-weighted cascade block-diagonal least-squares techniques and a structural model that incorporated anisotropic thermal parameters for all nonhydrogen atoms and isotropic thermal parameters for all hydrogen atoms. The six methyl groups were included in the refinement as idealized sp^3-rigid rotors. The remaining hydrogen atoms were fixed at idealized sp^2-hybridized positions with a C-H bond length of 0.96 Å.

Acknowledgment. Financial support from the Natural Sciences and Engineering Council of Canada and the Quebec Department of Education is acknowledged. S.M. thanks the Commonwealth Scholarship Fund for the award of a predoctoral fellowship. R.T. thanks the Natural Sciences and Engineering Council of Canada for the award of a predoctoral scholarship.

Supplementary Material Available: Full crystal structure analysis report (Table 4), Full tables of bond lengths and angles (Table 5), anisotropic temperature factors (Table 6), and hydrogen coordinates and temperature factors (Table 7) (11 pages); a listing of observed and calculated structure factor amplitudes for $[CpCoSCMe_3]_2$ (14 pages). Ordering information is given on any current masthead page.

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Proton NMR Spectroscopy of Flavocytochrome c_{552} from *Chromatium vinosum*†

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The anaerobic purple sulfur bacterium *Chromatium vinosum* utilizes sulfide, thiosulphate, or organic substrates as electron donors for phosphorylation.[1,2] It has been demonstrated that flavocytochrome c_{552} isolated from such a microorganism functions in vitro as a sulfide cytochrome *c* oxidoreductase and probably is the enzyme responsible for catalyzing the oxidation of sulfide to sulfur observed in vivo.[3,4]

The *C. vinosum* flavocytochrome c_{552} is one of the few proteins containing different types of redox prosthetic groups. There is still a controversy on the number of subunits composing the active enzyme and their molecular weights. Bartsch and co-workers reported the presence of three subunits tightly associated over the pH range 5-10: a covalently bound FAD- (through an 8-α-S cysteinyl linkage) containing subunit (42000 MW) and two smaller subunits (15000 MW) containing one heme-*c* each.[5-7] Yamanaka et al., conversely, suggested the flavocytochrome c_{552} to be composed by only two subunits, the flavin-containing one (46000 MW) and the other with the two hemes (21000 MW).[4,8]

Magnetic susceptibility measurements at neutral pH and low temperature indicate that the two heme irons are in a low-spin ground-state configuration ($S = 1/2$).[9,10] Mössbauer spectra point

† Abbreviations used throughout the paper: CD, circular dichroism; EPR, electron paramagnetic resonance; FAD, flavin adenine dinucleotide; NMR, nuclear magnetic resonance; ppm, parts per million; WEFT, water-eliminated Fourier transform.

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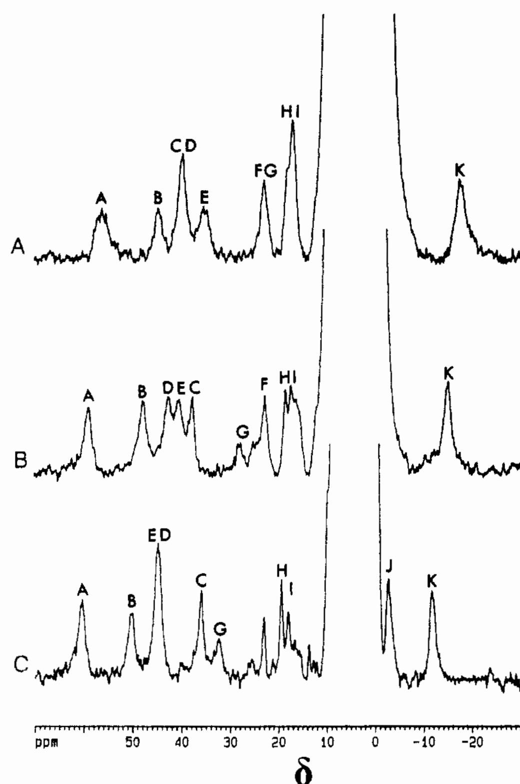

Figure 1. ^{1}H NMR spectra of flavocytochrome c_{552} from *C. vinosum* at pH 7.0 and 282 (A), 300 (B), and 323 (C) K.

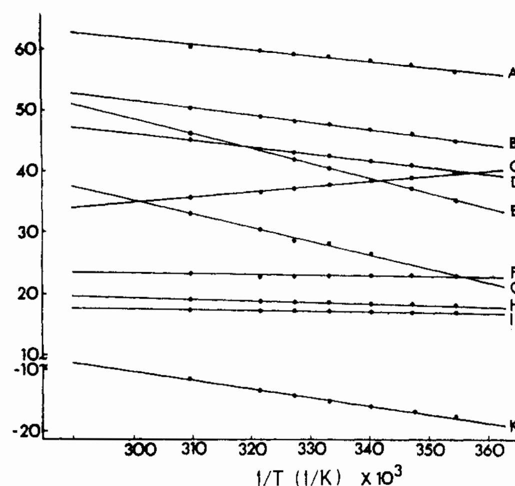

Figure 2. Temperature dependence of the ^{1}H NMR isotropically shifted resonances of flavocytochrome c_{552} from *C. vinosum* at pH 7.0.

out that the two heme moieties have an identical iron coordination whereas EPR experiments allow one to distinguish the two heme irons.[10,11] Furthermore, CD and resonance Raman studies suggested the existence of flavin–heme and heme–heme interactions inside the molecule.[7,8,12,13] In summary all the reports to date outline that the hemes and the flavin chromophores inside the protein are oriented to allow interactions between them and facilitate an internal fast electron transfer.

Nuclear magnetic resonance spectroscopy is a very powerful tool for the understanding of the molecular and electronic structure of biological molecules, since this technique is able to detect even very small variations in the local environment of a given nucleus. The electron spin density distribution is in fact controlled by the protein structure conformation and particularly, in the case of paramagnetic metalloproteins, by the unpaired electron-resonating nuclei interactions, which induce large hyperfine shifts to the signals of the nuclei in the near surroundings of the metal ions. Consequently, such resonances are very sensitive probes for the environment of the corresponding metal sites.[14]

We report here the ^{1}H NMR spectra of *C. vinosum* flavocytochrome c_{552} and definitely demonstrate the nonidentity of the two hemes. The irons' ground spin states at room temperature are discussed.

C. vinosum flavocytochrome c_{552} was purified by following the general procedure reported by Bartsch.[15-17] The absorbance ratio A_{280}/A_{410} ranged from 0.54 to 0.57, and the A_{480}/A_{520}, from 1.29 to 1.33. The pH values are not corrected for isotope effects. ^{1}H NMR spectra were recorded on a Bruker MSL 200 spectrometer operating at 200 MHz and equipped with a variable-temperature control unit accurate to ±0.1 °C. Typical spectra, with $\simeq$1 mM protein, were acquired by utilizing the super WEFT pulse sequence (180–τ–90–AQ) for suppressing the residual solvent signal through adjustment of the τ delay.[18] Peak shifts were referenced to the residual water signal. Chemical shifts are reported in parts per million (ppm).

In Figure 1 the spectra of the oxidized flavocytochrome c_{552} in D_2O at pH 7.0 and at 282, 300, and 323 K are reported. As expected, a number of hyperfine-shifted resonances are present downfield of 10 ppm. In analogy to previously reported spectra of heme proteins, these signals are generated by protons directly bound to the porphyrin rings, by the axial ligands, or by residues in the heme pockets. In particular, the heme ring methyl groups are expected to show relatively large downfield hyperfine shifts. From the spectra in Figure 1, it is evident that more than four resonances with relative intensity three are present in the downfield region and these signals may be attributed to heme methyl protons, indicating that the two heme moieties have a different environment. In addition, the further upfield methyl resonance K around −15 ppm suggests that at least one heme has methionine as the fifth iron axial ligand.[19-21] The resonance J around −2.8 ppm might also be tentatively assigned to a thioether methyl group.[19-21] The hyperfine shifts in the downfield region are larger than expected on the basis of an $S = 1/2$ system. This indicates that the average spin system is larger than $1/2$. The amount of high-spin heme present at room temperature, estimated on the basis of the largest downfield shifts for high-spin (70–80 ppm) and low-spin (20–30 ppm) heme systems,[14] is 60–75%. This holds at least for one heme group.

The temperature dependence of the shifts in cytochromes *c* is quite puzzling and not yet fully understood.[22-26] The temperature

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dependence of the shifts between 282 and 323 K for the present system is reported in Figure 2. All but one of the downfield hyperfine-shifted resonances move downfield as the temperature is raised. This is contrary to what expected on the basis of Curie's law. Three signals (A, B, and D) have similar slope. Possibly they belong to the same heme. The E and G signals are less shifted and have a steeper slope. They may belong to the second heme. Only few cytochromes *c* show anomalous temperature dependences of some of the hyperfine-shifted resonances.[22–25] Two mechanisms may account for such an anti-Curie behavior: quantum-mechanical spin admixing and spin equilibria involving two different spins.[14] The Curie behavior of the upfield signal indicates that such a group, presumably the $S-CH_3$ group, is involved in the equilibrium, for example through detachment or weakening of the Fe–S bond. It has already been suggested that detachment of $S-CH_3$ with increasing temperature induces high-spin species in horse ferricytochrome *c*.[26] The present system is another example of the variability of the temperature dependence of the shifts of low-spin ferricytochromes that exist in equilibrium with high-spin species. Finally, the NMR spectra at 300 K show that the more shifted resonances are not pH dependent in the range pH 5–10, indicating that the spin equilibrium is not regulated by ionization processes.

In conclusion, from the present data the two hemes appear clearly inequivalent and the presence on a moiety of at least one methionine as the fifth axial ligand is suggested. Furthermore, the presence of high- and low-spin species in thermal equilibrium and in an essentially fast exchange rate on the NMR time scale is proposed, with the low-spin species predominant at low temperatures.[9–11]

Registry No. Flavocytochrome c_{552}, 100091-97-2; iron, 7439-89-6; heme *c*, 26598-29-8; methionine, 63-68-3.

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Synthesis and Structure of a Novel Hexanuclear Iron(III) Complex Containing Six Terminal and Twelve Bridging Alkoxo Groups and One μ_6-Oxo Bridge

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One of the most striking properties of Fe(III) is its tendency to hydrolyze in aqueous solution where the final stage of hydrolysis usually is the formation of solid FeOOH.[2] It is, however, possible to isolate intermediate products, i.e., oxo- or hydroxo-bridged polynuclear compounds of well-defined composition, if suitable ligands for their coagulation or stabilization are used. The trinuclear oxo-centered carboxylates $Fe_3O(OOCR)_6L_3$ have been well-known for many years.[3] Recently, interest was focused on such complexes, due to their importance in biological systems.[4] A large variety of new polynuclears have been prepared, containing up to 16 Fe(III) atoms which are bridged by carboxylates, μ_2-, μ_3-, or μ_4-O, and μ_2- or μ_3-OH.[5] A central μ_5-O has also been postulated.[6] At the periphery, carboxylate or other suitable ligands are coordinated to iron(III) sites to prevent further polymerization. In particular, ligands providing an appropriate arrangement of three nitrogen or three oxygen atoms have been investigated for this purpose.[5,7] Such complexes usually were prepared in non-aqueous media under the influence of a weak base, followed by the addition of a limited amount of water. On the other hand, it is well-known that polyhydroxy compounds like sorbitol or sugars are able to solubilize Fe(III) in alkaline aqueous solutions.[4a,8] Due to the ubiquity of carbohydrates in biological systems, this phenomenon deserves increased attention. However, only little is known about the structure of such polynuclears.[9] In this contribution, we present the synthesis and the structure of the novel μ_6-O–Fe_6 core as protected by six fully deprotonated polyalcohol ligands. It seems that this is the first X-ray diffraction study reported on an iron(III) complex with a tridentate polyalkoxide as the only chelating ligand.

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Experimental Section

Preparation of $O[Fe(OCH_2)_3CCH_3]_6[N(CH_3)_4]_2 \cdot 4CH_3OH$. Tetramethylammonium hydroxide as a 25% in methanol solution (250 mL) was dried over molecular sieves by continous extraction of water in a N_2 atomosphere over a period of 3 weeks. The solvent was circulated by distillation and passed through a flask containing the drying agent. In this way, direct contact between the molecular sieves and the base was avoided. The molecular sieves were replaced by activated material every 3 days. The $N(CH_3)_4OCH_3$ solution (B) was used without further purification if the absorbance in the range 400–700 nm was negligible. Dry stock solutions of 2 M tris(hydroxymethyl)ethane (L) and of $FeCl_3$ (1.09 mmol/g) in methanol were kept under N_2.

Calculated amounts of these solutions (final concentrations [Fe] = 0.05 M, [B] = 0.5 M, and [L] = 0.3 M) were mixed under N_2, and a clear deep bluish green solution was obtained. Within 1 day, the color changed to light green and the precipitation of a bluish green solid was observed. After separation of the solid, the supernatant was yellow and contained 0.047 M total iron. Four samples of this solution were mixed with calculated amounts of water by the addition of a solution of H_2O (10 M) in methanol. The molar H_2O:Fe ratio was 0 (a), 2 (b), 10 (c), and 100 (d). In a fifth sample, pure water was added to a final content of 50% v/v (e). All of the five solutions remained clear, i.e., no precipitation of iron hydroxide could be observed. After a period of several weeks, brown or yellow crystals were observed in solutions a and b but were, however, unstable in air and too small for X-ray diffraction studies. Solution c was kept in the dark at ambient temperature. Within several months just one large single crystal had grown, which could be used for the X-ray structure analysis presented here.

Instrumentation and Physical Measurements. The magnetic susceptibility of the dry solution was measured by the Gouy method (Varian V 4005 electromagnet operating at 6 kG, Mettler ME 21 microbalance). An acidic aqueous solution of $FeCl_3$ was used for calibration, and the observed susceptibility was corrected for diamagnetism by using Pascal constants. For kinetic measurements, a Durrum Gibson stopped-flow spectrophotometer was used. Equal volumes of 4 M acetylacetone in CH_3OH and the complex solution were mixed (25° C) and the absorbance at 580 nm was monitored. The vis spectra were recorded on a Beckmann DB-GT spectrophotometer (400–700 nm).

Crystal Structure Determination. A piece with approximate dimensions of 0.83 × 0.95 × 0.63 mm was cut from the brown triclinic crystal obtained in solution c and sealed in a glass capillary, together with its

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