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 $\mu_6$-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, $\mu_2$-, $\mu_3$-, or $\mu_4$-O, and $\mu_2$- or $\mu_3$-OH.[5] A central $\mu_5$-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 $\mu_6$-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.

## 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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**Table I.** Crystallographic Data for $O[Fe(OCH_2)_3CCH_3]_6[N(CH_3)_4]_2{\cdot}4CH_3OH$

| | |
|---|---|
| chemical formula, fw | $C_{42}H_{94}Fe_6N_2O_{23}$, 1330.3 |
| space group | $P\bar{1}$ (No. 2) |
| *a*, *b*, *c*, Å | 12.541 (4), 12.904 (3), 11.564 (2) |
| α, β, γ, deg | 92.77 (1), 106.21 (2), 115.52 (2) |
| *V*, Å³ | 1590.7 (1.7) |
| *Z* | 1 |
| *T*, °C | 22 |
| λ(Mo Kα), Å | 0.71073 |
| $\rho_{calcd}$, g cm$^{-3}$ | 1.389 |
| μ(Mo Kα), cm$^{-1}$ | 12.44 |
| transm coeff | 0.374–0.501 |
| $R(F_o)$, $R_w(F_o)$ | 0.0597, 0.0714 |

**Table II.** Atomic Coordinates and Isotropic or Equivalent Isotropic Temperature Factors with Estimated Standard Deviations in Parentheses for Non-Hydrogen Atoms of $O[Fe(OCH_2)_3CCH_3]_6[N(CH_3)_4]_2{\cdot}4CH_3OH$

| atom | *x* | *y* | *z* | $U_{eq}/U_{iso}$,[a] Å² |
|---|---|---|---|---|
| Fe(1) | 0.41780 (6) | 0.42515 (6) | 0.14671 (6) | 0.0404 (1) |
| Fe(2) | 0.61948 (6) | 0.67817 (6) | 0.12410 (6) | 0.0407 (1) |
| Fe(3) | 0.65332 (6) | 0.45088 (6) | 0.07055 (6) | 0.0416 (1) |
| O(11) | 0.5000 (0) | 0.5000 (0) | 0.0000 (0) | 0.0425 (9) |
| O(12) | 0.5304 (3) | 0.5903 (3) | 0.2365 (3) | 0.0467 (6) |
| O(13) | 0.4637 (3) | 0.6974 (3) | 0.0496 (3) | 0.0454 (6) |
| O(14) | 0.7033 (3) | 0.8223 (3) | 0.2356 (3) | 0.0566 (8) |
| O(22) | 0.7957 (3) | 0.4264 (3) | 0.1315 (4) | 0.0625 (8) |
| O(23) | 0.7423 (3) | 0.6152 (3) | 0.1704 (3) | 0.0453 (7) |
| O(24) | 0.7120 (3) | 0.5279 (3) | −0.0633 (3) | 0.0450 (6) |
| O(32) | 0.5650 (3) | 0.3894 (3) | 0.1900 (3) | 0.0486 (6) |
| O(33) | 0.3288 (3) | 0.2761 (3) | 0.0203 (3) | 0.0473 (7) |
| O(34) | 0.3573 (3) | 0.3523 (3) | 0.2666 (3) | 0.0613 (8) |
| C(11) | 0.4993 (5) | 0.7664 (4) | 0.2673 (5) | 0.054 (1) |
| C(12) | 0.4844 (5) | 0.6477 (4) | 0.3011 (4) | 0.052 (1) |
| C(13) | 0.4259 (5) | 0.7492 (5) | 0.1309 (5) | 0.059 (1) |
| C(14) | 0.6381 (5) | 0.8552 (5) | 0.2980 (5) | 0.057 (1) |
| C(15) | 0.4418 (6) | 0.8144 (5) | 0.3433 (5) | 0.075 (1) |
| C(21) | 0.9177 (4) | 0.6279 (5) | 0.1016 (5) | 0.050 (1) |
| C(22) | 0.9162 (5) | 0.5173 (5) | 0.1459 (5) | 0.064 (1) |
| C(23) | 0.8709 (4) | 0.6868 (4) | 0.1792 (5) | 0.048 (1) |
| C(24) | 0.8422 (4) | 0.6008 (5) | −0.0359 (4) | 0.053 (1) |
| C(25) | 1.0548 (5) | 0.7152 (6) | 0.1185 (6) | 0.074 (2) |
| C(31) | 0.4027 (5) | 0.1946 (4) | 0.1971 (5) | 0.058 (1) |
| C(32) | 0.5406 (5) | 0.2757 (4) | 0.2154 (5) | 0.058 (1) |
| C(33) | 0.3224 (5) | 0.1715 (4) | 0.0628 (5) | 0.057 (1) |
| C(34) | 0.3559 (5) | 0.2443 (5) | 0.2844 (5) | 0.063 (1) |
| C(35) | 0.3926 (7) | 0.0760 (5) | 0.2278 (6) | 0.083 (2) |
| N(41) | 0.7983 (4) | 0.5842 (4) | 0.5212 (4) | 0.059 (1) |
| C(42) | 0.8203 (7) | 0.7030 (6) | 0.4964 (7) | 0.094 (2) |
| C(43) | 0.8592 (7) | 0.5924 (8) | 0.6539 (6) | 0.102 (2) |
| C(44) | 0.6611 (5) | 0.5069 (6) | 0.4880 (5) | 0.068 (1) |
| C(45) | 0.8474 (7) | 0.5318 (7) | 0.4446 (7) | 0.098 (2) |
| C(s1) | 0.168 (1) | 0.7328 (9) | 0.525 (1) | 0.051 (3) |
| O(s1) | 0.217 (1) | 0.8462 (9) | 0.504 (1) | 0.099 (4) |
| C(s2) | 0.766 (1) | 0.1530 (8) | 0.1414 (9) | 0.116 (4) |
| O(s2) | 0.8168 (6) | 0.2527 (6) | 0.2322 (6) | 0.093 (2) |
| C(s3) | 0.024 (3) | −0.011 (3) | 0.753 (2) | 0.164 (11) |
| O(s3) | 0.054 (1) | 0.019 (1) | 0.648 (2) | 0.120 (5) |

[a] Solvent molecules were refined isotropically. $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i^*{\cdot}a_j^*{\cdot}\mathbf{a}_i{\cdot}\mathbf{a}_j$.

mother liquor. Data collection was performed on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromatized Mo Kα radiation. The lattice parameters were obtained by least-squares refinement of the setting angles of 24 automatically centered reflections with $11.2 \le \theta \le 14.5°$. A total of 9004 intensities were collected by using the $\omega$–$2\theta$ scan technique with variable scan speeds of 1.04–8.24°/min (maximal measuring time per reflection: 50 s). Three standard reflections were checked at an interval of every 3 h; no significant decrease of intensities was noted. Four reflections were collected every 300 reflections to control crystal orientation. The data were corrected for Lorentz and polarization effects and a numerical absorption correction based on eight indexed crystal faces was applied with SHELX76.[10] The structure was solved by the Patterson interpretation routine of SHELXS86[11] and refined with anisotropic displacement parameters for all non-hydrogen atoms of the complex and the cation. The methyl hydrogen atoms were treated as rigid groups whereas the $CH_2$ hydrogen atoms were refined riding on the corresponding carbon atoms with common isotropic displacement parameters for each ligand. The non-hydrogen atoms of four solvent molecules could be located in the difference Fourier maps. However, the C–O distances appeared to be relatively short (1.27–1.34 Å). Therefore, these molecules were refined with constrained bond lengths of 1.396 ± 0.004 Å and estimated occupancy factors of 0.5 for the atoms C(s1), O(s1), C(s3), O(s3). Neutral scattering factors for H, C, N, and O atoms were those from SHELX76;[10] that for Fe was from ref 12. The least-squares refinements were carried out by minimizing $\sum w(|F_o| - |F_c|)^2$, $w = 1$ (unit weights). The structure determination parameters are given in Table I, atom coordinates are listed in Table II, and selected bond lengths and a summary of bond angles are presented in Tables III and IV, respectively.

**Table III.** Selected Bond Lengths (Å) of $O[Fe(OCH_2)_3CCH_3]_6[N(CH_3)_4]_2{\cdot}4CH_3OH$ with Estimated Standard Deviations in Parentheses

| | | | |
|---|---|---|---|
| Fe(1)–Fe(2) | 3.235 (1) | Fe(1)–Fe(2′) | 3.169 (1) |
| Fe(1)–Fe(3) | 3.201 (1) | Fe(1)–Fe(3′) | 3.168 (1) |
| Fe(1)–O(11) | 2.270 (1) | Fe(1)–O(12) | 1.997 (3) |
| Fe(1)–O(24′) | 1.994 (4) | Fe(1)–O(32) | 2.028 (4) |
| Fe(1)–O(33) | 2.012 (3) | Fe(1)–O(34) | 1.866 (4) |
| Fe(2)–Fe(3) | 3.195 (1) | Fe(2)–Fe(3′) | 3.158 (2) |
| Fe(2)–O(11) | 2.259 (1) | Fe(2)–O(12) | 2.021 (4) |
| Fe(2)–O(13) | 2.030 (4) | Fe(2)–O(14) | 1.885 (4) |
| Fe(2)–O(23) | 1.995 (4) | Fe(2)–O(33′) | 1.982 (4) |
| Fe(3)–O(11) | 2.234 (1) | Fe(3)–O(13′) | 1.983 (3) |
| Fe(3)–O(22) | 1.895 (5) | Fe(3)–O(23) | 2.020 (3) |
| Fe(3)–O(24) | 2.020 (4) | Fe(3)–O(32) | 1.992 (4) |

**Table IV.** Summarized Bond Angles for $O[Fe(OCH_2)_3CCH_3]_6{}^{2-}$

| type of angle | no. | range, deg | av value, deg |
|---|---|---|---|
| *fac*-Fe–Fe–Fe | 12 | 59.10–61.50 | 60.00 |
| *mer*-Fe–Fe–Fe | 6 | 89.09–90.92 | 90.00 |
| *trans*-Fe–O(11)–Fe | 3 | 180.00 | 180.00 |
| *cis*-Fe–O(11)–Fe | 12 | 88.84–91.16 | 90.00 |
| Fe–$O_{bridg}$–Fe | 12 | 103.8–107.2 | 105.2 |
| O(11)–Fe–$O_{term}$ | 6 | 173.0–173.8 | 173.5 |
| O(11)–Fe–$O_{bridg}$ | 24 | 80.7–84.2 | 82.4 |
| $O_{term}$–Fe–$O_{bridg}$ | 24 | 92.9–102.4 | 97.6 |
| *cis*-$O_{bridg}$–Fe–$O_{bridg}$ | 24 | 85.3–91.4 | 89.0 |
| *trans*-$O_{bridg}$–Fe–$O_{bridg}$ | 12 | 166.0–163.4 | 164.6 |

**Table V.** Characteristic Interatomic Distances (Å) in $M_6O_{19}$ Cores

| | $Mo_6O_{19}{}^{2-}$ | $W_6O_{19}{}^{2-}$ | $OFe_6[(O_3CH_2)_3CCH_3]_6{}^{2-}$ |
|---|---|---|---|
| M–$O_{cent}$ | 2.31–2.32 | 2.32–2.33 | 2.23–2.27 |
| M–$O_{bridg}$ | 1.86–2.00 | 1.89–1.95 | 1.99–2.03 |
| M–$O_{term}$ | 1.68 | 1.67–1.71 | 1.86–1.89 |
| M–M | 3.26–3.29 | 3.28–3.30 | 3.16–3.23 |

## Results and Discussion

For all solutions of the Fe–L system (L = $CH_3C(CH_2O)_3$) with various $H_2O$ content (0–50%), very similar vis spectra were recorded with a characteristic shoulder at 470 nm and a strong increase of the absorbance below 450 nm, indicating that polymers already formed under non-aqueous conditions.[13] This result is in agreement with the observed magnetic susceptibility (average $\mu_{eff} = 4.35\ \mu_B$, 295 K).[6] There is evidence, however, that a variety of different polynuclears are present in solution: the kinetics of formation of the iron(III) tris (acetylacetonate) was investigated in the presence of a large excess of acetylacetone by the stopped-flow technique. The multiple-phase kinetics provided unambigous indication for a variety of polynuclears in this solute.[14]

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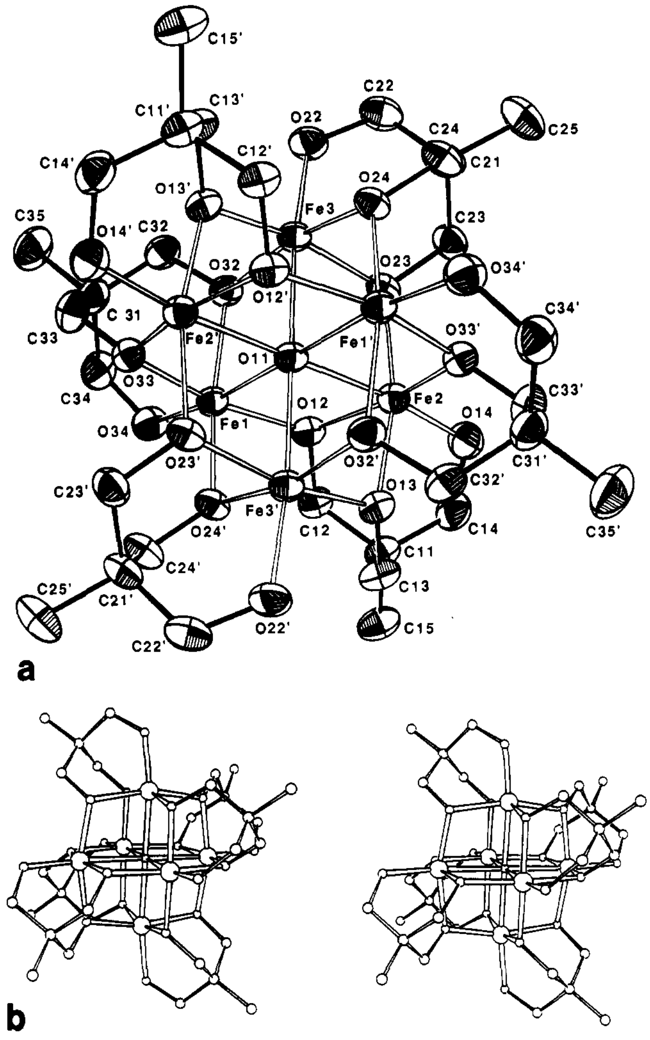

**Figure 1.** (a) ORTEP drawing of $O[Fe(OCH_2)_3CCH_3]_6^{2-}$ with numbering scheme and vibrational ellipsoides at the 50% probability level. (b) Stereoview of the compound.

Hence it must be taken into account that the crystal isolated does not represent the major solute component.

In the centrosymmetric $O[Fe(OCH_2)_3CCH_3]_6^{2-}$ complex, a central O(-II) is octahedrally surrounded by six Fe(III) atoms. This $OFe_6$ aggregate is encapsulated by a hydrophobic shell of six fully deprotonated, facially coordinated $CH_3C(CH_2O)_3^{3-}$ entities, and the Fe(III) atoms are located each in the center of a distorted octahedron of six oxygen atoms, forming a $Fe_6O_{19}$ unit as shown in Figure 1. The 19 oxygen atoms are of three types—central O, bridging RO, and terminal RO. The structure of this $Fe_6O_{19}$ core is closely related to the polyoxoanions $M_6O_{19}^{2-}$ of the early transition metals (Table V).[15] Considering the similar ionic radii of Fe(III), Mo(VI) and W(VI),[16] this analogy is quite understandable. However, the lower charge of Fe(III) requires the presence of alkoxo-groups instead of O(-II) as bridging and terminal ligands. The long bond distance between the Fe atoms and the central oxygen atom (Table III) is remarkable and does not fit in the common range of Fe-O bond lengths. However, elongated Fe-O bonds are formed, when the coordination number of the central oxygen atom increases from 2 to 4 as demonstrated in the sequence $\mu_2$-O, 1.79 Å (in $Fe_2O(O_2CR)_2L_2$);[7a] $\mu_3$-O, 1.92 Å (in $Fe_3O(O_2CR)_6L_3$);[17] and $\mu_4$-O, 2.03 Å (in $Fe_{16}CoO_{10}(OH)_{10}(O_2CPh)_{20}$.[5b] Hence, the observed average value of 2.25 Å for CN = 6 seemingly extends this series.

The formation of a polynuclear complex, starting with a Fe:L ratio of 1:6, is surprising and demonstrates the high nucleophility of alkoxo groups. Consequently, the formation of mononuclear complexes requires alkoxides with lower basicity. For perfluoropinacole (p$K$ = 5.95), the formation of the mononuclear tris chelate in water has been reported,[18] and recent investigations revealed mononuclear Fe(III) complexes with substituted cyclohexanetriols (p$K$ = 8.14)[19] in aqueous solution.[20]

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**Supplementary Material Available:** Tables SI-SV, listing crystallographic data, anisotropic displacement parameters of non-hydrogen atoms, positional parameters of hydrogen atoms, and bond distances and angles and a stereoview of the unit cell (13 pages); a table of calculated and observed structure factors (16 pages). Ordering information is given on any current masthead page.

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## Chelate Binding Preferences in $CpML_4$ Complexes: Preparation and Structure of *trans*-$(\eta^5\text{-}C_5H_5)Mo[(C_6F_5)_2PCH_2CH_2P(C_6F_5)_2](CO)Cl$

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### Introduction

Complexes of the general formula $CpML_n$ are ubiquitous to organometallic chemistry and constitute an important class of "coordinatively compact" systems intermediate between metallocene ($Cp_2ML_x$) and classic $L_nM$ coordination compounds. $CpML_4$ complexes in particular may be considered to be electronically seven-coordinate as well as sterically pseudo-five-coordinate, and have been the subject of numerous theoretical,[1] structural,[1-3] and dynamic[4] studies. Although $CpML_4$ coordination

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