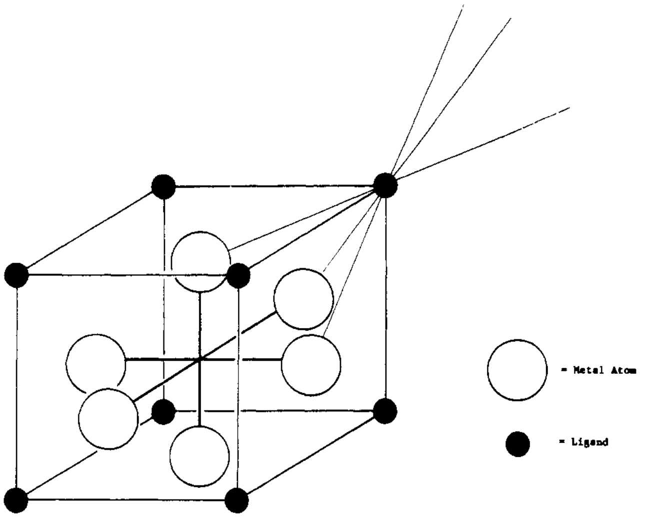

**Figure 4.** Diagram showing three different potential orientations of $M_2$ units within a cubic array of ligands. Note how the three M–L bonds diverge considerably as they extend out from the cube.

from having a molecule lying at 90° to the correct direction can be severe enough to make this kind of misorientation energetically impossible—at least to a detectable degree.

In the case of $M_2X_4(PR_3)_4$ molecules where the R groups are $C_3H_7$ or $C_4H_9$, there is enough flexibility ("slop") in the collection of three of these, that they can compensate for the misorientation of the 3-fold axes of the $PR_3$ units by deploying the outer two or three carbon atoms on each one in a somewhat disordered fashion. There are indeed always either observable disorder or very large displacement parameters observed in these cases. The fact that each of the three possible orthogonal directions for the molecules is observed to a different extent is simply due to the fact that each of these directions is distinct (nonequivalent) in the crystal, so that the extents to which "slop" in the phosphine ligands can compensate for the misorientation relative to the neighbors are, naturally, different for each one. We would, finally, draw the conclusion that, for all $M_2X_4(PR_3)_4$ molecules where R = $C_3H_7$ or any longer $C_nH_{2n+1}$ chain, 2- or most likely 3-fold disorder is to be expected in these crystals.

We are left with now only one observation to explain: Namely, why do the $M_2X_4(PEt_3)_4$ compounds show not only 3-fold disorder of the $M_2$ units but statistical disordering of the X and $PEt_3$ groups over the eight vertices of the quasi-cube? One answer—which really is not an answer—is that the $M_2X_4(PEt_3)_4$ molecules lie on crystallographic sites of cubic symmetry and hence both of these disorders are demanded. However, this simply raises the question of why the molecules are capable of packing in this way. This is a question to which we have no concrete answer. Evidently, the $M_2X_4(PEt_3)_4$ molecules have lost the "knobbiness" of the $M_2X_4(PMe_3)_4$ molecules and become smoother without, however, having achieved the "sloppiness" of those with the larger R groups. They represent that kind of special case that is often extremely difficult to explain in chemistry.

**Acknowledgment.** We thank the National Science Foundation for financial support and Dr. Larry R. Falvello for assistance with some of the X-ray crystallography.

**Supplementary Material Available:** For compound **1**, a complete table of positional and thermal parameters and, for all five crystal structures, full tables of crystal parameters and details of data collection and refinement, bond distances, bond angles, and anisotropic displacement parameters and ORTEP diagrams (44 pages); tables of observed and calculated structure factors (80 pages). Ordering information is given on any current masthead page.

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# Notes

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## Model Studies Related to Hemerythrin. Synthesis and Characterization of a Bridged Tetranuclear Iron(III) Complex

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Oligomeric oxo-bridged iron complexes have been found to mediate a variety of functions in biology.[1] Of particular interest are the proteins known or presumed to contain an oxo-bridged diiron core in their active site: hemerythrin,[2-4] purple acid phosphatase,[5] ribonucleotide reductase,[6] and methane monooxygenase.[7,8] Of these proteins, the main structural features of the functional center in hemerythrin are those that are best understood. As such, it continues to be a focus of extensive chemical and physical studies, not only because it is of intrinsic interest but also because it is considered prototypical of diiron proteins about which much less is known.

One of the more interesting features to emerge from recent hemerythrin-directed model studies is an appreciation for the facility with which many of these form iron aggregates of a nuclearity higher than two.[9-12] In many cases, the factors that govern the formation of a particular iron oligomer are still poorly understood, and as such, the actual structure formed from a particular ligand system can be difficult to predict. For instance, in a recent report,[13] Wieghardt et al. proposed the stabilization of a ($\mu$-oxo)bis($\mu$-acetato)diiron(III) core using Takamoto's[14] 1,2-bis(1,4,7-triaza-1-cyclononyl)ethane ligand system ($L_1$) as the

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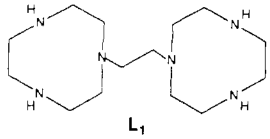
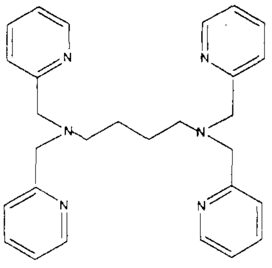
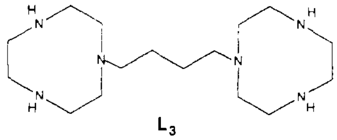


$L_1$





$L_3$

$L_2$

capping subunit. However, in a later report,[10d] Toftlund et al. suggested, on the basis of his studies with tetrakis(2-pyridylmethyl)-1,4-butanediamine ($L_2$), that this Wieghardt complex might better be formulated as a tetranuclear species. Our own analysis of CPK space-filling models suggested that an ethylene-bridged triazacyclononane-derived ligand system would be too congested to support the formation of a diiron core and that a four-carbon bridge would be a more promising candidate. We have, therefore, synthesized a new ligand system, 1,4-bis(1,4,7-triaza-1-cyclononyl)butane ($L_3$), in high yield and explored its ability to stabilize a diiron core similar to that found in hemerythrin. Interestingly, however, we found that this butyl-bridged system stabilizes the formation of a tetranuclear species $[Fe_2(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2(L_3)]_2^{4+}$ in the solid state, for which, to our knowledge, there is only one direct literature precedent.[10d]

## Experimental Section

NMR spectra were obtained in $CDCl_3$ with $Me_4Si$ as an internal standard and recorded on a General Electric QE-300 spectrometer. Routine electron impact (EI) mass spectra were measured with a Finnigan MAT 4023 or a Bell and Howell 21-110B instrument. Chemical ionization mass spectrometric analyses (CI MS) were also made using the MAT 4023 instrument. Infrared spectra were recorded, as KBr pellets, from 4000 to 400 $cm^{-1}$ on a Bio-Rad FTS-40 spectrophotometer. Electronic spectra were recorded in acetonitrile on a Beckman DU-7 spectrophotometer. HBr/AcOH (30%) was purchased from Aldrich Chemical Co.

**1-(*p*-Tolylsulfonyl)-1,4,7-triazacyclononane (2).** 1,4,7-Tris(*p*-tolylsulfonyl)-1,4,7-triazacyclononane[15] (**1**) (37.0 g; 62.6 mmol) and phenol (44 g) were dissolved in 500 mL of 30% HBr/AcOH. The solution was then heated at 90 °C for 36 h. The white precipitate that formed was filtered off and washed with ether. This solid was dissolved in 1 N NaOH (solution pH > 12) and extracted with chloroform. The organic layers were combined and dried over $MgSO_4$. The $MgSO_4$ was removed by filtration and the solvent removed in vacuo to afford pure **2** (16.1 g) as a white solid: yield 90.9%; mp 82–84 °C; $^1H$ NMR $\delta$ 1.80 (2 H, br, N$H$), 2.33 (3 H, s, C$H_3$Ar), 2.79 (4 H, s, HNC$H_2$C$H_2$NH), 2.98 (4 H, m, $ArNCH_2$C$H_2$NH), 3.09 (4 H, m, ArNC$H_2$$CH_2$NH), 7.22 (2 H, dd, aromatic), 7.59 (2 H, dd, aromatic); $^{13}C$ NMR $\delta$ 21.19, 49.36, 49.58, 53.55, 126.97, 129.42, 135.70, 142.95; CI MS *m/e* 284 ($MH^+$).

**1,4-Bis(*p*-tolylsulfonyl)-1,4,7-triazacyclononane (3).** To a room-temperature, vigorously stirred suspension of **2** (2.76 g; 9.75 mmol) in 10 mL of 7.5 N NaOH was added dropwise TsCl (1.86 g; 975 mmol) dissolved in 100 mL of diethyl ether. After 3 h, the solvent was removed on a rotary evaporator. The resulting white solid was taken up in chloroform, the solution was washed with water, and the organic layer was dried over $MgSO_4$. The $MgSO_4$ was filtered off, the solvent removed in vacuo, and the product recrystallized from ethanol to afford pure **3** (3.5 g) as white crystals: yield 82.1%; mp 217–218 °C (lit.[13,16] mp 195–197 °C); $^1H$ NMR $\delta$ 1.59 (1 H, br, N$H$), 2.41 (6 H, s, C$H_3$Ar), 3.14–3.20 (8 H, br, $ArNCH_2$C$H_2$NH), 3.43 (4 H, s, ArNC$H_2$C$H_2$NAr), 7.30 (4 H, dd, aromatic), 7.65 (4 H, dd, aromatic); $^{13}C$ NMR $\delta$ 21.38, 49.01, 52.96, 53.81, 127.15, 129.70, 135.38, 143.48; CI MS *m/e* 438 ($MH^+$).

**1,4-Bis[4,7-bis(*p*-tolylsulfonyl)-1,4,7-triaza-1-cyclononyl]butane (5). Method a.** To a stirred solution of compound **3** (1.80 g; 4.12 mmol) and triethylamine (1 mL) in 50 mL of freshly distilled dichloromethane was added succinyl chloride (0.32 g; 2.06 mmol). The solution was stirred at room temperature under a nitrogen atmosphere for 15 min, at which time 1 N NaOH (10 mL) was added. The organic layer was separated and dried over $MgSO_4$. Pure diamide, **4**, (1.89 g) was obtained by column chromatography on silica gel (2% MeOH/$CHCl_3$, eluent): yield 96.0%; $^1H$ NMR $\delta$ 2.38 (6 H, s, C$H_3$Ar), 2.41 (6 H, s, C$H_3$Ar), 2.84 (4 H, s, NC(O)C$H_2$), 3.19–3.83 (24 H, m, -NC$H_2$-), 7.25 (4 H, dd, aromatic), 7.30 (4 H, dd, aromatic), 7.60 (4 H, dd, aromatic), 7.66 (4 H, dd, aromatic); $^{13}C$ NMR $\delta$ 21.42, 28.79, 49.72, 50.47, 50.66, 51.30, 51.98, 53.93, 127.23, 127.38, 129.72, 129.81, 134.05, 134.25, 143.79, 173.56.

**Table I.** Crystallographic Data for $[(C_{16}H_{36}N_6)_2Fe_4O_2(CH_3CO_2)_4](PF_6)_4$ (**6a**) and $[(C_{16}H_{36}N_6)_2Fe_4O_2(CH_3CO_2)_4](PF_6)_4{\cdot}(CH_3CN)_2$ (**6b**)

| | **6a** | **6b** |
|---|---|---|
| chem formula | $C_{40}H_{84}N_{12}O_{10}Fe_4P_4F_{24}$ | $C_{44}H_{90}N_{14}O_{10}Fe_4P_4F_{24}$ |
| *a*, Å | 11.376 (2) | 11.457 (2) |
| *b*, Å | 23.352 (3) | 13.338 (4) |
| *c*, Å | 13.328 (2) | 23.943 (7) |
| $\beta$, deg | 107.910 (12) | 97.35 (3) |
| *V*, Å$^3$ | 3369.2 (9) | 3629 (2) |
| *Z* | 2 | 2 |
| fw | 1696.42 | 1778.53 |
| space group | $P2_1/n$ (No. 14) | $P2_1/c$ (No. 14) |
| *T*, °C | −75 | −75 |
| λ(Mo K$\alpha$), Å | 0.7107 | 0.7107 |
| $\rho_{calcd}$, g/cm$^3$ (−75 °C) | 1.67 | 1.63 |
| $\mu$, $cm^{-1}$ | 10.58 | 9.869 |
| transm coeff | 0.7530–0.8898 | 0.7976–0.9503 |
| *R*(*F*) | 0.0480 | 0.1210 |
| $R_w(F)$ | 0.0540 | 0.0979 |

**Method b.** To a flame-dried, 100-mL round-bottomed flask was added a 1 M solution of $LiAlH_4$ in THF (15 mL). Diamide **4** (1.10 g; 1.15 mmol) dissolved in dry $CH_2Cl_2$ (15 mL) was added dropwise while the solution temperature was kept at 0 °C under $N_2$. The reaction was allowed to come to room temperature and then stirred overnight. Following quenching with sodium sulfate decahydrate, the solvent was removed on a rotary evaporator. The resulting solid was partitioned between $CHCl_3$ and 1 N NaOH. The organic layer was then separated off and dried over $MgSO_4$. Pure **5** was then obtained in quantitative yield following removal of the solvent on the rotary evaporator and drying in vacuo: mp 166–169 °C; $^1H$ NMR $\delta$ 1.45 (4 H, br, $CH_2$C$H_2$C$H_2$$CH_2$), 2.40 (12 H, s, C$H_3$Ar), 2.53 (4 H, t, C$H_2$$CH_2CH_2$C$H_2$), 2.83 (8 H, br, $CH_2N$(C$H_2$)$_2$), 3.17 (8 H, br, ArNC$H_2$N($CH_2$)$_2$), 3.48 (8 H, s, ArNC$H_2$C$H_2$NAr), 7.28 (8 H, dd, aromatic), 7.65 (8 H, dd, aromatic); $^{13}C$ NMR $\delta$ 21.23, 25.69, 51.36, 52.50, 55.77, 57.23, 127.07, 129.53, 135.74, 143.08; CI MS *m/e* 929 ($MH^+$).

**1,4-Bis(1,4,7-triaza-1-cyclononyl)butane ($L_3$).** The tetratosyl derivative, **5**, (1.04 g; 1.12 mmol) was dissolved in concentrated $H_2SO_4$ (10 mL) and heated at 90 °C under a nitrogen atmosphere for 48 h. The resulting brown solution was cooled in an ice bath and basified to a solution pH > 12 by the cautious addition of 15 N NaOH. It was then extracted with $CHCl_3$ (3 × 250 mL). The resulting organic layers were then combined and dried over $MgSO_4$. Following removal of solvent, ligand $L_3$ was obtained as a colorless oil, which solidified upon refrigeration: yield 0.32 g (91.5%); $^1H$ NMR $\delta$ 1.43 (4 H, br, -$CH_2$C$H_2$C$H_2$$CH_2$-), 2.46–2.55 (12 H, cluster, N(C$H_2$)$_3$), 2.64–2.74 (16 H, cluster, HNC$H_2$-), 2.85 (4 H, br, N$H$); $^{13}C$ NMR $\delta$ 25.62, 46.24, 46.47, 52.58, 57.27; EI MS *m/e* 312 ($M^+$); HR MS *m/e* 312.2994 ($M^+$) (calcd for $C_{16}H_{36}N_6$, *m/e* 312.3001).

**Preparation of $[Fe_2(L_3)(\mu\text{-}O)(\mu\text{-}CH_3CO_2)_2]_2(PF_6)_4$ (6).** To a solution of $L_3$ (48.2 mg) in ethanol (15 mL) was added $FeCl_3{\cdot}6H_2O$ (83.5 mg). The resulting yellow precipitate was collected by filtration, washed with ethanol, and dissolved in a saturated aqueous solution of ammonium acetate (5 mL). To the resulting deep brown solution was added an excess of $KPF_6$ (60 mg). This led to the formation of an orange-brown precipitate that was collected on a fine-fritted glass filter funnel and washed with ethanol; yield 81.4 mg (62.2%). Green (**6a**) and orange (**6b**) crystals were obtained by vapor diffusion of methanol into an acetonitrile solution of **6** and were separated from one another by mechanical means. IR (KBr, $cm^{-1}$, selected peaks): 3656 (w), 3332 (m), 3110 (w), 1559 (s), 1456 (s), 840 (vs), 738 (m), 557 (s). UV/vis: see Table II. Anal. Calcd for $C_{40}H_{84}F_{24}Fe_4N_{12}O_{10}P_4$: C, 28.30; H, 4.99; N, 9.91. Found: C, 28.25; H, 5.00; N, 9.87. Complexes **6a** and **6b** were further characterized by X-ray crystallography (see below and Figures 1 and 2).

**Crystal Structures of $[(C_{16}H_{36}N_6)_2Fe_4O_2(CH_3CO_2)_4](PF_6)_4$ (6a) and $[(C_{16}H_{36}N_6)_2Fe_4O_2(CH_3CO_2)_4](PF_6)_4{\cdot}2CH_3CN$ (6b).** Structure solutions and refinement were effected using the procedures, programs, and parameters reported earlier.[17] The data crystal for **6a** was a green block

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(16) As previously reported,[13] compound **3** was found to have a melting point of 197–198 °C. In our hands, compound **3** gave a melting point of 217–218 °C.

**Table II.** Structural (Å and deg) and Spectroscopic Data for Complexes **6**–**9** and Azidomethemerythrin

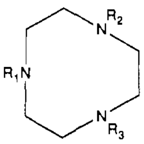
| | **6** | **7** | **8** | azidomethemerythrin | **9** |
|---|---|---|---|---|---|
| Fe–O | 1.793 (3), 1.761 (3) | 1.781 (4) | 1.800 (3) | 1.79 | 1.794 (3) |
| Fe–N, cis (av) | 2.126 (2) | 2.166 (13) | 2.198 (4) | 2.13 | 2.136 (11) |
| Fe–N, trans | 2.268 (3) | 2.205 (7) | 2.268 (6) | 2.24 | 2.307 (5) |
| Fe···Fe, within core | 3.076 (1) | 3.063 (2) | 3.12 (4) | 3.23 | 3.129 (2) |
| Fe···Fe, between cores | 7.604 (1),[a] 7.933 (9)[b] | | | | 7.469 (2) |
| Fe–O–Fe | 119.84 (14) | 118.7 (4) | 119.7 (1) | 130 | 121.3 (3) |
| $\lambda_{max}$, nm[c] ($\epsilon$, $cm^{-1}$ (mol of $Fe)^{-1}$ L) | 739 (111) | 745 (71) | 734 (60) | 680 (95) | 730 (78.5) |
| | 551 (sh) | 554 (sh) | 550 (sh) | | |
| | 513 (563) | 508 (sh) | 519 (600) | | |
| | | 492 (sh) | | | |
| | 471 (745) | 468 (655) | 475 (780) | 446 (1850) | 505 (493) |
| | 423 (sh) | 420 (sh) | 428 (500) | | 470 (554) |
| | | 368 (sh) | | 380 (sh) | |
| | 338 (3818) | 333 (3682) | 345 (5250) | 326 (3375) | 348 (3678) |
| | | 280 (sh) | | | |
| ref | this work | 19, 20 | 21 | 3, 4 | 10d |

[a] **6a**. [b] **6b**. [c] Solvents: **6** and **7**, acetonitrile; **8**, water; **9**, not reported.

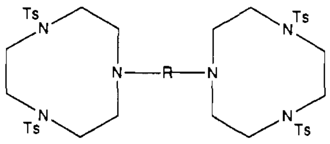
that was cut from a larger crystal and had approximate dimensions 0.18 × 0.20 × 0.23 mm, while the data crystal for **6b** was an orange plate of approximate dimensions 0.05 × 0.23 × 0.36 mm. Data for both were collected at −75 °C on a Nicolet R3 diffractometer, equipped with a graphite monochromator and a Nicolet LT-2 low-temperature delivery system (Table I). The crystal system for **6a** is monoclinic, and the space group is $P2_1/n$ (No. 14) as uniquely determined from systematically absent reflections. The structure was solved by direct methods and refined by full-matrix least squares in blocks of 288 and 284 parameters with the scale factor refined in each block. All hydrogen atoms except the methyl hydrogens were located from a difference electron density map. Methyl hydrogens were calculated in idealized positions (C–H = 0.96 Å). Hydrogen atoms were refined with isotropic thermal parameters except those of C22 which were fixed at $1.2U_{eq}$ of C22. The crystal system for **6b** is monoclinic, and the space group is $P2_1/c$ (No. 14) as uniquely determined from systematically absent reflections. The structure was solved by direct methods and refined by full-matrix least squares with anisotropic thermal parameters for the Fe, P, F, and O atoms. Attempts to refine the remaining non-hydrogen atoms with anisotropic thermal parameters resulted in many atoms with nonpositive definite temperature factors. All the hydrogens were calculated in idealized positions (C–H = 0.96 Å) with isotropic thermal parameters fixed at $1.2U$ of the relevant atom. The high values for $R$ and $R_w$ are due to the small size and poor crystal quality of the data crystal and to the high thermal motion of the atoms of the butyl group linkage. Both complexes, **6a** and **6b**, lie around an inversion center.

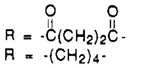
## Results and Discussion

The new ligand, 1,4-bis(1,4,7-triaza-1-cyclononyl)butane ($L_3$), was prepared in high yield by using a three-stage synthetic sequence. First, 1,4-bis(*p*-tolylsulfonyl)-1,4,7-triazacyclononane (**3**),



**1** $R_1 = R_2 = R_3 = Ts$
**2** $R_1 = Ts, R_2 = R_3 = H$
**3** $R_1 = R_2 = Ts, R_3 = H$



**4** 
$R = -\overset{\overset{O}{\|}}{C}(CH_2)_2\overset{\overset{O}{\|}}{C}-$

**5** $R = -(CH_2)_4-$

which was prepared from the tritosylate (**1**) via the monotosylate (**2**), was reacted with succinyl chloride to form the pertosylated diamide intermediate (**4**).[18] Compound **4** was then reduced in nearly quantitative yield to give the protected diamine (**5**) by using $LiAlH_4$. All four sulfonamide protecting groups were then removed through hydrolysis using concentrated sulfuric acid to reveal the target, $L_3$.

The iron(III) complex of $L_3$ was formed by using a method similar to that of Wieghardt et al.[19] Specifically, addition of 2 equiv of ferric chloride hexahydrate to an ethanolic solution containing 1 equiv of $L_3$ led to the immediate formation of a yellow precipitate. Dissolution of this precipitate in a saturated aqueous solution of ammonium acetate afforded a clear brown solution. Following addition of potassium hexafluorophosphate, an orange-brown precipitate, **6**, was isolated. Crystals suitable for X-ray analysis were grown by diffusion of methanol into an acetonitrile solution of **6**.

Interestingly, two differently colored crystals, green (**6a**) and orange (**6b**) (with a predominance of green), were formed during this crystallization procedure. Both crystal types were structurally characterized and found to contain the same basic tetranuclear cation complex. The orange crystals contained two molecules of acetonitrile per unit cell, whereas the green crystals contained no solvent molecules at all. However, we do not consider this difference in solid-state composition to be responsible for the intriguing difference in the colors in these two ostensibly similar systems. Dissolution of either crystal set into acetonitrile gives solutions of identical color (deep orange) and spectra. Similarly, when dried in vacuo, both sets of crystals gave identical analyses (within error). However, and this is considered critical, drying the solvated orange crystals of **6b** does not alter their color or appearance. This suggests that the 2 molar equiv of acetonitrile originally present in the crystal lattice was not, in and of itself, responsible for the nongreen color. Rather, it appears that it is differences in the unit cell packing (which the presence of such solvent molecules could induce) that are responsible for the variations in the observed solid-state color.

X-ray structural analyses of **6a** and **6b** revealed that in both cases a tetranuclear complex is formed. Figure 1 shows the X-ray structure of the cationic core of **6a**, and Figure 2 shows an overlay of the two cationic cores derived from the X-ray structure analysis of the two different crystals (green and orange). In both structures, each of the four iron atoms lies in the center of an approximate octahedral coordination environment comprising one facially coordinated triazacyclononane ring, one $\mu$-oxo ligand, and two $\mu$-acetato ligands. However, the four-carbon chain does not link two iron centers by bridging the $\mu$-oxo, bis($\mu$-acetato) core as one might except for dimer formation. Rather, two dinuclear core units are linked via the four-carbon bridge so as to form a tetranuclear complex.

The structural and spectroscopic features of the diiron core of **6a** (which are essentially identical with those of **6b**; cf. above) are summarized in Table II along with comparable data for azidomethemerythrin[3,4] and two other well-characterized hemerythrin model systems of the general formula $[Fe_2(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2L_2]^{2+}$ (L = 1,4,7-triazacyclononane[19,20] (**7**) and 1,4,7-trimethyl-1,4,7-triazacyclononane[21] (**8**)). The bond lengths and bond angles found

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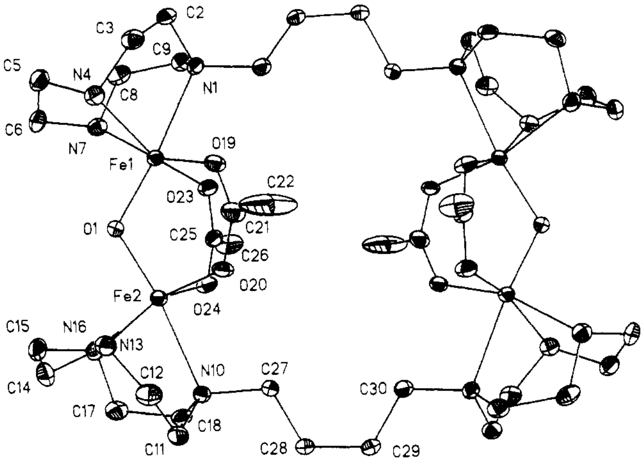

**Figure 1.** View of the cation of **6a**, showing the atom-labeling scheme. Thermal ellipsoids are scaled to 30% probability level. H atoms are of an arbitrary size. The complex lies on an inversion center with the geometry around the Fe atoms being distorted octahedral. The average Fe-N(tertiary amine) bond lengths (2.268 (3) Å) are slightly longer than the averate Fe-N(secondary amine) bond lengths (2.126 (2) Å). The average Fe-acetate bond lengths are 1.979 (2) Å, while the oxo-bridge bond lengths are asymmetric with Fe(1)-O(1) = 1.793 (3) Å and Fe(2)-O(1) = 1.761 (3) Å.

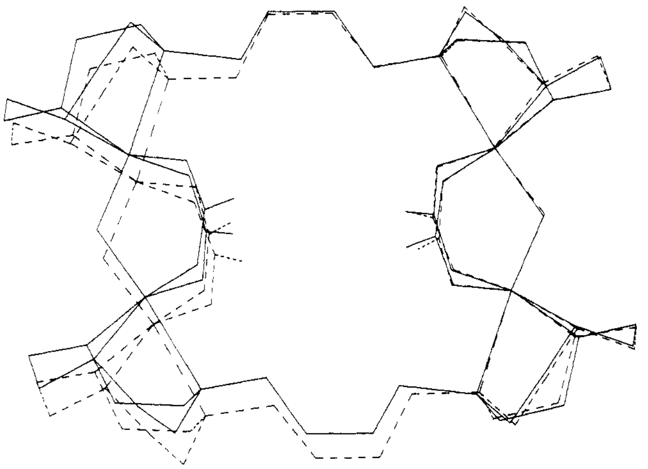

**Figure 2.** Comparison of the cations of **6a** and **6b**. The coordination sphere of oxo-bridged dimer in **6a** (shown by dotted line) is fitted by least-squares to the equivalent atoms in **6b** (solid lines), highlighting the nearly identical geometry around the Fe atoms.

in the (μ-oxo)bis(μ-acetato)diiron(III) core of **6a** (and **6b**) are quite similar to those reported for complexes **7** and **8** and also, to a lesser extent, azidomethemerythrin itself. In particular, the Fe···Fe distance (3.076 (1) Å) in the diiron core of **6** lies somewhat between that formed in complexes **7** (3.063 (2) Å) and **8** (3.12 (4) Å). Notably, however, unlike those of the simple dimers, the diiron cores in **6a** (and **6b**) are asymmetrical (Fe(1)-O(1) = 1.793 (3) Å; Fe(2)-O(1) = 1.761 (3) Å). We attribute this to constraints placed on the diiron core by the tetramethylene bridge.

Structural and spectroscopic data for Toftlund's related tetranuclear complex, derived from ligand $L_2$ (**9**),[10d] are also reported in Table II for comparison with **6**. Both complexes **6** and **9** contain a tertiary nitrogen trans to the μ-oxo bridge; as a result, the bridging acetates from each diiron core are directed toward the center of the molecule. The preference for this structure over dimer formation has been attributed to the *trans* disposition of the tertiary nitrogen atom and the μ-oxo ligand in each diiron core unit.[10d] In fact, in **6** the acetate methyl groups on opposite diiron cores are an approximate van der Waals radius apart. The Fe···Fe distances between core units in **6** (7.604 (1) and 7.933 (9) Å for **6a** and **6b**, respectively) are, therefore, considerably larger than the comparable Fe···Fe distance in **9** (7.469 (2) Å). These minor differences aside, it is worth noting that both ligands $L_2$ and $L_3$ contain two distinct binding sites separated by a four-carbon chain and they both stabilize similar tetrameric iron(III) cores, *rather than the corresponding dimeric iron(III) complexes.* This finding, in our opinion, serves not only to suggest further[10d] that the iron(III) complex formed from $L_1$[13] might well be tetrameric in nature but also to underscore the difficulty inherent in preparing viable hemerythrin models by using loosely linked alkyl-bridged ligand systems. As such, the present results may have important implications in terms of preparing improved model systems.

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**Supplementary Material Available:** Figures showing the structure of cation **6b**, giving atom-labeling schemes, and unit cell packing diagrams for cations **6a** and **6b** (Figures S1-S3), tables listing positional and isotropic or equivalent isotropic thermal parameters for the non-hydrogen atoms of **6a** and **6b** (Tables S1 and S6, respectively), positional and isotropic thermal parameters for the hydrogen atoms of **6a** and **6b** (Tables S2 and S7, respectively), anisotropic thermal parameters for the non-hydrogen atoms of **6a** and **6b** (Tables S3 and S8, respectively), bond lengths and angles for the non-hydrogen atoms of **6a** and **6b** (Tables S4 and S9, respectively), bond lengths and angles for the hydrogen atoms of **6a** (Tables S5 and S10, respectively), and complete crystallographic summaries for systems **6a** and **6b** (Table S11), and text describing experimental X-ray details for **6a** and **6b** (42 pages); tables of observed and calculated structure factor amplitudes (Tables S12 and S13) (72 pages). Ordering information is given on any current masthead page.

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## Crystal and Molecular Structure of Bis[1,3-bis(diphenylphosphino)propane]platinum(0): A Reevaluation

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Despite a current active interest in the catalytic, electronic, and luminescent properties of homoleptic platinum(0) phosphine derivatives,[1,2] there have been remarkably few of these complexes crystallographically characterized. The reported structures include $[Pt(PPh_3)_3]$,[3] $[Pt(triphos)_2]$ [triphos = 1,1,1-tris(diphenylphosphinomethyl)ethane; $(Ph_2PCH_2)_3CCH_3$],[4] $[Pt_2(\mu\text{-dppm})_3]$ [dppm = bis(diphenylphosphino)methane; $Ph_2PCH_2PPh_2$],[5] and $[(dbpp)Pt{=}Pt(dbpp)]$ [dbpp = 1,3-bis(di-*tert*-butylphosphino)propane; $(Me_3C)_2PCH_2CH_2CH_2P(CMe_3)_2$].[6] Of these, only $[Pt(triphos)_2]$ contains a $\{Pt^0P_4\}$ geometry, and the unsymmetrical

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