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Synthesis, Structure Determination, and Stereoisomerism of Dirhodium(I) Tetracarbonyl Tropocoronand Complexes

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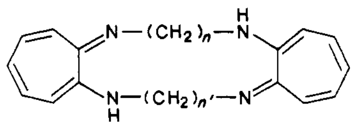
The reaction of $[Rh(CO)_2Cl]_2$ with Li_2(TC-5,5), the lithium salt of the tropocoronand ligand containing two aminotropone iminate groups linked by two pentamethylene chains, produces an isomeric pair of compounds, *syn*-$[Rh_2(CO)_4$(TC-5,5)] (*syn*-**1**), in which the metal atoms are held on the same face of the macrocyclic ligand, and *anti*-**1**, in which the dicarbonylrhodium(I) moieties lie on opposite sides of the tropocoronand. Synthesis, purification, and X-ray structural analyses of these "invertomers" are reported along with infrared and proton and carbon-13 NMR spectroscopic data. The four-coordinate square-planar rhodium atoms have mean Rh–N and Rh–C bond lengths of 2.025 (5) and 1.848 (8) Å, respectively. The metals are separated by a distance of 5.892 (1) Å in *anti*-**1** and by 4.392 (4) Å in the syn isomer. Crystal data for *anti*-**1**: monoclinic, space group $P2_1/c$, $a = 15.252$ (3) Å, $b = 15.270$ (2) Å, $c = 11.859$ (3) Å, $\beta = 95.13$ (2)°, $V = 2751.0$ Å^3, $Z = 4$, $R_1 = 0.044$. Crystal data for *syn*-**1**: monoclinic, space group $C2/m$, $a = 14.849$ (3) Å, $b = 16.466$ (4) Å, $c = 11.280$ (4) Å, $\beta = 95.05$ (3)°, $V = 2747.1$ Å^3, $Z = 4$, $R_1 = 0.031$. Proton NMR spectral studies showed that no isomerization occurs on the NMR time scale up to a temperature of 130 °C, from which a lower limit of $\Delta G^\ddagger > 20$ kcal/mol was estimated for the interconversion barrier between stereoisomers. Thermal conversion of isomerically pure samples to a mixture of invertomers could be achieved by prolonged heating for several hours at 130 °C, however.

Introduction

We have been investigating the coordination chemistry of tropocoronands $H_2(TC\text{-}n,n')$, macrocyclic ligands formed by



(TC-*n*,*n*′)H_2

n,*n*′ = 3,3; 4,4; 4,5; 5,5; 6,6

joining two aminotropone iminate groups by polymethylene linker chains.[1] Apart from mononuclear Cu(II)[2] and Ni(II)[3] complexes, in which the metal geometries are largely dictated by the specific tropocoronand used, we have also obtained binuclear compounds $[Cu_2(\mu\text{-}OAc)(\mu\text{-}OMe)$(TC-6,6)],[4] $[Cu_2(\mu$-alkyne)(TC-6,6)],[5] and $[Cu_2(CO)_2$(TC-5,5)].[6] Homobinuclear complexes of this kind, as well as heterobinuclear analogues in asymmetric macrocycles such as the phosphands,[7] are of potential interest for promoting unusual organometallic syntheses or catalysis. Their stereochemical properties have also proved to be intriguing.

In the (μ-alkyne)dicopper(I) tropocoronand complexes, the metal atoms were held on the same side of the macrocycle, but in the case of the $[Cu_2(CO)_2$(TC-5,5)] compound, the carbonylcopper(I) units were situated far apart and on opposite sides of the ligand. Since the former configuration favors reactions involving bimetallic activation, we wondered whether complexes involving these two forms of the ligand could be thermally interconverted. The $[Cu_2(CO)_2$(TC-5,5)] complex was thermally too unstable for carrying out studies of this kind. We have therefore prepared and studied the analogous dicarbonylrhodium(I) compounds in order both to expand the scope of tropocoronand coordination chemistry and to obtain molecules stable enough for studying the thermal stability of the syn and anti "invertomers". Conformational isomerism of this kind has previously been considered for bimetallic complexes of binucleating macrocyclic ligands.[8]

Table I. ^{13}C NMR Chemical Shifts for *syn*- and *anti*-$[Rh_2(CO)_4$(TC-5,5)] (*syn*- and *anti*-**1**)[a]

carbon[b]	*syn*-**1**	*anti*-**1**	carbon[b]	*syn*-**1**	*anti*-**1**
11	166.49	166.96	31	58.85	57.04
12	113.49	113.61	32	29.93	32.00
13	132.46	132.82	33	30.25	27.18
14	120.14	120.34			

[a] Recorded at 75.5 MHz from solutions in CD_2Cl_2. [b] See Figures 2 and 4 for atom labels.

In this article, we report synthetic, structural, spectroscopic, and stereochemical studies of new homobinuclear rhodium(I) dicarbonyl tropocoronand complexes in which two stereoisomers result from the conformational preferences of the coordinating macrocycle.

Experimental Section

General Methods. The tropocoronand macrocycle $[H_2$(TC-5,5)] was synthesized by a published method.[1b] $[Rh(CO)_2Cl]_2$ was prepared according to a literature procedure[9] and stored in a desiccator. Carbon monoxide gas (CP grade) was supplied by Matheson. All other reagents were purchased from Aldrich Chemical Co. Tetrahydrofuran (THF) solvent was distilled from sodium benzophenone ketyl and degassed with nitrogen or argon for 15 min prior to use. Standard Schlenk techniques were used in handling all air-sensitive compounds and reaction mixtures. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories (Woodside, NY). Proton and carbon-13 NMR spectral analyses were carried out on a Bruker 250 or Varian XL-300 FT instrument with deuteriochloroform, methylene-d_2 chloride, or *o*-xylene-d_{10} solutions. Chemical shifts are reported in parts per million downfield from tetramethylsilane (TMS), and coupling constants are reported in hertz. Infrared spectra (KBr) were recorded on an IBM Instruments IR/32 FTIR spectrophotometer.

Synthesis of Anti and Syn Isomers of $[Rh_2(CO)_4$(TC-5,5)] (1). A flame-dried round-bottomed flask containing $[Rh(CO)_2Cl]_2$ (58.6 mg, 0.151 mmol) was charged with 10 mL of THF under an atmosphere of carbon monoxide. The presence of excess CO helps to stabilize [Rh-

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Table II. Experimental Details of the X-ray Diffraction Studies of *anti*- and *syn*-[$Rh_2(CO)_4$(TC-5,5)] (*anti*- and *syn*-**1**)[a]

	anti-**1**	*syn*-**1**
formula	$C_{28}H_{30}N_4O_2Rh_2$	$C_{28}H_{30}N_4O_2Rh_2$
a, Å	15.252 (3)	14.849 (3)
b, Å	15.270 (2)	16.466 (4)
c, Å	11.859 (3)	11.280 (4)
β, deg	95.13 (2)	95.05 (3)
V, Å^3	2751.0	2747.1
FW	692.39	692.39
Z	4	4
ρ_{calcd}, g cm^{-3}	1.672	1.674
ρ_{obsd},[b] g cm^{-3}	1.672 (2)	1.668 (3)
space group	$P2_1/c$	$C2/m$
radiation	Mo Kα (0.71069 Å)	Mo Kα
data limits, deg	$3 \leqslant 2\theta \leqslant 55$	$3 \leqslant 2\theta \leqslant 55$
linear abs coeff, cm^{-1}	11.15	11.17[c]
no. of unique reflcns	6292	3264
no. of abs data	3553	2281
criterion	$F > 4\sigma(F)$	$F > 6\sigma(F)$
no. of params refined	345	180
R_1[d]	0.044	0.031
R_2[e]	0.055	0.045

[a] Data were collected by $\omega/2\theta$ scans on an Enraf-Nonius CAD-4F κ-geometry diffractometer at 22 °C. Calculations were performed on a DEC VAX 11/780 computer by using SHELX-76. [b] Measured by neutral buoyancy in aqueous NaI solution. [c] An empirical absorption correction was applied. [d] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [e] $R_2 = [\sum w||F_o| - |F_c||^2/\sum w|F_o|^2]^{1/2}$.

$(CO)_2Cl]_2$; a black precipitate forms when the reaction is carried out without CO. The mixture was cooled to −78 °C, and with vigorous stirring, a THF solution of Li_2(TC-5,5), prepared from 50.7 mg (0.135 mmol) of H_2(TC-5,5) and *n*-butyllithium (2.0 equiv), was added dropwise by a syringe. The reaction mixture was allowed to warm to room temperature and stirred for an additional 20 min. The reaction vessel was flushed with N_2 to remove excess CO, and the red solution was filtered under a positive pressure of inert gas. Evaporation of solvent in vacuo left a red, air-stable solid. Analysis of the ^{1}H NMR spectrum of this soluble mixture in deuteriochloroform revealed a ca. 1:1 ratio of the anti and syn isomers (vide infra) of [$Rh_2(CO)_4$(TC-5,5)]. Recrystallization of the mixture from pentane/toluene solvent mixtures at −20 °F gave a mixture of dark red opaque crystals and light red amorphous, but well-shaped, solids. The latter showed no X-ray diffraction and contained no lattice solvent. A similar mixture was obtained from methanol/chloroform at room temperature. The combined yield was 52.3 mg (56%). The two types of crystals were easily separated from one another manually as they grew in separate homogeneous clumps. Pure crystals of the anti isomer suitable for X-ray diffraction studies were obtained at room temperature from methanol/chloroform solvent mixtures. Anal. Calcd for $C_{28}H_{30}N_4O_4Rh_2$: C, 48.57; H, 4.37; N, 8.09. Found: C, 48.26; H, 4.36; N, 8.13. IR (KBr, cm^{-1}): 2939 (w), 2040 and 1970 (s, C≡O), 1589 (m), 1508 (s), 1481 (m), 1444 (s), 1422 (s), 1386 (s), 1330 (w), 1275 (m), 1233 (m), 1045 (w), 722 (m). ^{1}H NMR (300 MHz, *o*-xylene-d_{10}, 293 K): δ 6.79 (4 H, dd, J = 11.7, 8.9), 6.60 (4 H, d, J = 10.8), 6.23 (2 H, t, J = 9.0), 4.02 (4 H, d, J = 14.0), 3.57 (4 H, dd, J = 12.6, 8.6), 1.50–1.17 (12 H, complex m). Table I lists the ^{13}C NMR chemical shifts of the ligand carbons of *anti*-**1**.

Since the light red amorphous solids obtained from pentane/toluene solvent mixtures gave no diffraction, well-formed, analytically pure crystals of the syn isomer were obtained, instead, from methanol/toluene solvent mixtures at room temperature. Anal. Calcd for $C_{28}H_{30}N_4O_4Rh_2$: C, 48.57; H, 4.37; N, 8.09. Found: C, 48.82; H, 4.55; N, 8.04. IR (KBr, cm^{-1}): 2939 (m), 2044 and 1981 (s, C≡O), 1589 (m), 1508 (s), 1483 (m), 1445 (s), 1421 (s), 1386 (s), 1336 (w), 1276 (m), 1233 (m), 1045 (w), 722 (m). ^{1}H NMR (300 MHz, *o*-xylene-d_{10}, 293 K): δ 6.48 (4 H, dd, J = 11.7, 8.6), 6.36 (4 H, d, J = 11.1), 5.91 (2 H, t, J = 9.1), 4.08 (4 H, d, J = 14.5), 3.84 (4 H, t, J = 11.8), 2.44 (2 H, quartet of triplets, J = 13.0, 4.0), 1.61–1.32 (10 H, complex m). Carbon-13 NMR chemical shifts are listed in Table I.

X-ray Structural Work. Details of the data collection, reduction, and refinement are summarized in Table II. Typical procedures employed in our laboratory are further described in ref 10. Unit cell parameters were refined by using the setting angles of 25 reflections having $2\theta > 30°$. Standard reflections monitored every 3600 s of exposure time showed no crystal decay. An empirical absorption correction was applied to the data for *syn*-**1**. Owing to the more regular crystal size, data for *anti*-**1** were not corrected for absorption.

***anti*-[$Rh_2(CO)_4$(TC-5,5)] (*anti*-1).** Rectangular crystals of *anti*-**1** were obtained by slow diffusion of methanol into a chloroform solution of the complex at room temperature. A red crystal of dimensions 0.2 × 0.2 × 0.3 mm was placed in a capillary for the diffraction study. Open-counter ω scans of low-angle reflections revealed sharp ($\overline{\Delta\omega_{1/2}}$ = 0.24°) featureless profiles. The space group $P2_1/c$ (C_{2h}^5, No. 14)[11a] was chosen from the systematic absences, a choice later confirmed by the solution and successful refinement of the structure. Standard Patterson and difference Fourier techniques were used to locate the non-hydrogen atoms of the structure. The refinement included fixed, calculated positions (C–H = 0.95 Å) for all hydrogen atoms, which were then allowed to "ride" on their respective carbon atoms. Each group of hydrogen atoms was given a common isotropic temperature factor, which converged at U = 0.178 (17) Å^2 for the aminotroponeiminate ring hydrogen atoms and U = 0.108 (7) Å^2 for the methylene protons. Non-hydrogen atoms were refined anisotropically. The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = 1.6298/[\sigma^2(F_o) + 0.000625(F_o)^2]$. Scattering factors for neutral atoms and corrections for anomalous dispersion were taken from ref 12, and hydrogen atom scattering factors from ref 13. The highest peak on the final difference Fourier map was 1.19 e Å^{-3} near the center of an aminotroponeiminate ring; the next highest peak was 0.50 e Å^{-3}.

***syn*-[$Rh_2(CO)_4$(TC-5,5)] (*syn*-1).** Thin red rectangular columns of *syn*-**1** were grown by slow diffusion of methanol into concentrated solutions of the complex dissolved in toluene at room temperature. A crystal of dimensions 0.15 × 0.16 × 0.38 mm was selected and mounted at the end of a glass fiber. The crystal quality was checked by open-counter ω scans of several low-angle reflections, which showed no unusual features ($\overline{\Delta\omega_{1/2}}$ = 0.15°). Study on the diffractometer revealed a *C*-centered monoclinic system with no other systematic absences. The structure was solved by the heavy-atom method and difference Fourier maps. The choice of space group $C2/m$ (C_{2h}^3, No. 12), one of three consistent with the systematic absences,[11b] was confirmed by the successful refinement of the structure. Aromatic and aliphatic hydrogen atoms were treated in the same manner as for *anti*-**1** (see above) with thermal parameters converging at U = 0.099 (8) Å^2 and U = 0.075 (4) Å^2 for the ring and methylene chain hydrogens, respectively. As with the *anti*-**1** refinement, anisotropic temperature factors were used for all non-hydrogen atoms. The same weighted function was minimized with $w = 1.6884/[\sigma^2(F_o) + 0.000625(F_o)^2]$. The highest peak on the final difference Fourier map was 0.74 e/Å^3, near a rhodium atom.

NMR Experiments. *o*-Xylene-d_{10} (Aldrich) was used as received to dissolve a sample consisting of approximately a 1:1 mixture of syn and anti isomers of **1**. The solution was filtered into an 8-in. NMR tube (Wilmad 526PP), frozen in liquid N_2, and sealed under vacuum. Spectra were recorded at 19, 130, and again at 19 °C. The two room-temperature spectra were identical.

Results

Synthesis. When a THF solution of the dilithium salt of the tropocoronand-5,5, Li_2(TC-5,5), was allowed to react with [$Rh(CO)_2Cl]_2$ under a CO atmosphere at low temperature, equimolar amounts of *syn*- and *anti*-[$Rh_2(CO)_4$(TC-5,5)] were formed.[14] The infrared spectrum of the product revealed the presence of terminally coordinated, cis carbonyl ligands,[15] somewhat broadened and suggestive of a mixture. That a mixture of products was obtained was further evident from the ^{1}H NMR spectrum, which was much more complex than anticipated from previous experience.[5,6] Moreover, the ^{13}C NMR spectrum revealed 14 resonances, twice the number expected for a symmetrical [$Rh_2(CO)_4$(TC-5,5)] compound. Finally, two types of crystals were evident following recrystallization of the product mixture. Pu-

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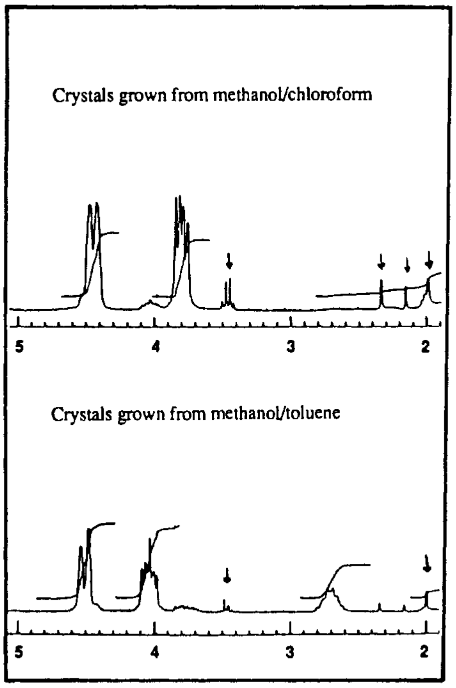

Figure 1. α-Methylene proton resonances for the anti (top) and syn (bottom) isomers of $[Rh_2(CO)_4(TC\text{-}5,5)]$. Peaks designated by arrows are impurities. Spectra were observed at 250 MHz ($CDCl_3$).

Table III. Final Positional Parameters for *anti*-$[Rh_2(CO)_4(TC\text{-}5,5)]$ (*anti*-**1**)[a]

ATOM	X	Y	Z	Bequiv
Rh1	0.79544(3)	0.82819(3)	0.59215(4)	3.56(2)
Rh2	0.73214(4)	0.12437(4)	0.89279(5)	4.46(2)
O1	0.8583(4)	0.6986(4)	0.7699(5)	6.5(3)
O2	0.9864(3)	0.8611(4)	0.5727(6)	7.6(3)
O3	0.5761(5)	0.1290(5)	0.0285(8)	10.6(5)
O4	0.6626(5)	0.2905(4)	0.7859(6)	9.4(4)
N1	0.6632(3)	0.8110(3)	0.5949(5)	3.8(2)
N2	0.7473(3)	0.9100(3)	0.4679(4)	3.7(2)
N3	0.7812(3)	0.0078(4)	0.9493(4)	3.8(3)
N4	0.8459(4)	0.1155(3)	0.8177(5)	4.3(3)
C1	0.8323(4)	0.7481(5)	0.7043(6)	4.6(3)
C2	0.9137(5)	0.8482(5)	0.5807(6)	4.8(4)
C3	0.6346(6)	0.1276(6)	0.9751(8)	6.6(5)
C4	0.6920(6)	0.2278(6)	0.8278(8)	6.6(5)
C11	0.6118(4)	0.8558(4)	0.5159(6)	3.8(3)
C12	0.5187(4)	0.8517(5)	0.5138(7)	5.1(4)
C13	0.4538(5)	0.8843(6)	0.4349(8)	6.1(4)
C14	0.4598(6)	0.9306(6)	0.3389(8)	6.7(5)
C15	0.5342(6)	0.9614(5)	0.2987(7)	6.0(4)
C16	0.6205(5)	0.9541(5)	0.3444(6)	5.2(4)
C17	0.6600(4)	0.9084(4)	0.4400(5)	3.6(3)
C21	0.8610(5)	0.9804(4)	0.9093(6)	4.7(3)
C22	0.8917(5)	0.8972(5)	0.9362(6)	5.1(4)
C23	0.9696(6)	0.8575(5)	0.9216(7)	5.9(4)
C24	0.0444(5)	0.8931(5)	0.8724(7)	5.1(4)
C25	0.0482(5)	0.9721(6)	0.8217(7)	5.7(4)
C26	0.9810(5)	0.0401(5)	0.8062(7)	5.6(4)
C27	0.8971(4)	0.0432(5)	0.8436(5)	4.1(3)
C31	0.6239(4)	0.7592(4)	0.6794(6)	4.4(3)
C32	0.5973(4)	0.8124(4)	0.7790(6)	4.4(3)
C33	0.6764(4)	0.8505(4)	0.8514(6)	4.3(3)
C34	0.6475(4)	0.9068(5)	0.9452(6)	4.5(3)
C35	0.7298(4)	0.9507(5)	0.0217(6)	4.8(3)
C41	0.8029(5)	0.9693(5)	0.4072(6)	4.5(3)
C42	0.7969(5)	1.0644(4)	0.4489(6)	4.6(3)
C43	0.8377(5)	1.0732(5)	0.5694(6)	5.1(4)
C44	0.8222(5)	0.1672(4)	0.6187(6)	5.3(4)
C45	0.8690(5)	0.1819(5)	0.7348(7)	5.4(4)

[a] Numbers in parentheses are errors in the last significant digit(s). See Figure 2 for atom-labeling scheme.

rification of the two isomers was achieved by a combination of mechanical separation, solubility differences in toluene, in which the syn isomer is more soluble, and recrystallization.

The purified complexes exhibited greatly simplified ^1H NMR spectra, displayed in Figure 1. The key difference between the two samples is the symmetrical multiplet centered at δ 2.69, corresponding to two hydrogens, which occurs in the spectrum of only one isomer. The ^{13}C NMR spectra of the purified isomers exhibit only seven signals apiece, as expected, the chemical shifts of which are listed in Table I. This spectroscopic evidence is consistent with the occurrence of syn and anti isomers of $[Rh_2(CO)_4(TC\text{-}5,5)]$, in which the rhodium atoms are situated on the same or on opposite faces of the macrocycle, respectively.

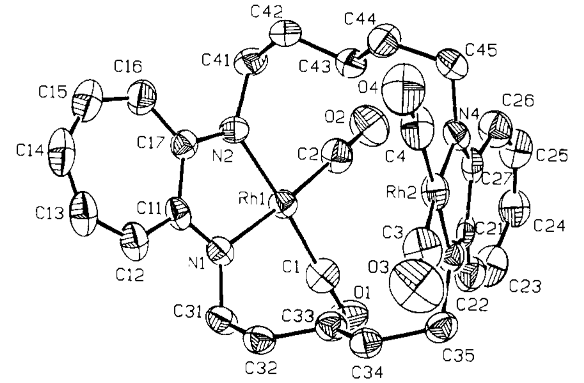

Figure 2. Structure of *anti*-**1**, showing the 50% probability thermal ellipsoids and atom-labeling scheme.

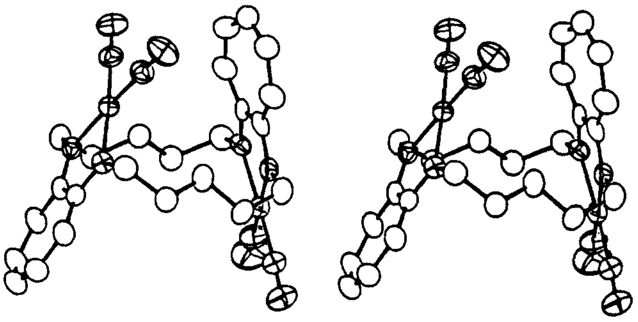

Figure 3. Stereoview of the structure of *anti*-**1**.

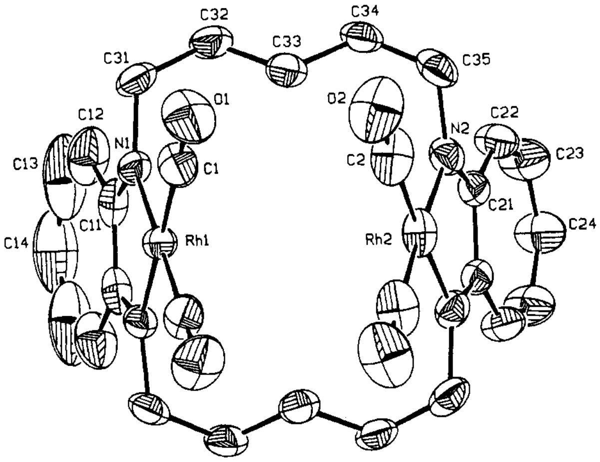

Figure 4. Structure of *syn*-**1**, showing the 50% probability thermal ellipsoids and atom-labeling scheme.

Crystal and Molecular Structures. Final coordinates for non-hydrogen atoms of *anti*-**1** are given in Table III. Interatomic distances and bond angles are listed in Table IV. Tables V and VI list the positional parameters for all non-hydrogen atoms and the interatomic bond lengths and angles of *syn*-**1**, respectively. A listing of the non-hydrogen atom temperature factors, hydrogen atom parameters, and observed and calculated structure factors for both isomers may be found in the supplementary material, Tables S1–S6.

As expected from the spectral data, $[Rh_2(CO)_4(TC\text{-}5,5)]$ occurs as two stereoisomers, anti (Figures 2 and 3) and syn (Figures 4 and 5), in which the $\{Rh(CO)_2\}$ moieties are situated on opposite sides of the mean plane through the tropocoronand macrocycle and on a common face of the ligand, respectively. The rhodium atoms have four-coordinate, square-planar stereochemistry with two nitrogen donor atoms from the aminotroponeiminate groups

Table IV. Interatomic Distances (Å) and Angles (deg) for *anti*-[$Rh_2(CO)_4$(TC-5,5)] (*anti*-**1**)[a]

Rh1 —— Rh2	5.892(1)		
Rh1 - C1	1.856(7)	Rh2 - C3	1.85(1)
Rh1 - C2	1.846(7)	Rh2 - C4	1.838(9)
Rh1 - N1	2.036(5)	Rh2 - N3	2.021(5)
Rh1 - N2	2.019(5)	Rh2 - N4	2.025(6)
N1 - C11	1.353(8)	N3 - C21	1.408(9)
N1 - C31	1.449(9)	N3 - C35	1.494(9)
N2 - C17	1.343(8)	N4 - C27	1.370(9)
N2 - C41	1.472(9)	N4 - C45	1.477(9)
C1 - O1	1.131(9)	C3 - O3	1.14(1)
C2 - O2	1.140(9)	C4 - O4	1.15(1)
C11 - C17	1.453(9)	C21 - C27	1.38(1)
C11 - C12	1.419(9)	C21 - C22	1.38(1)
C12 - C13	1.39(1)	C22 - C23	1.36(1)
C13 - C14	1.35(1)	C23 - C24	1.43(1)
C14 - C15	1.35(1)	C24 - C25	1.35(1)
C15 - C16	1.38(1)	C25 - C26	1.46(1)
C16 - C17	1.419(9)	C26 - C27	1.39(1)
C31 - C32	1.52(1)	C41 - C42	1.54(1)
C32 - C33	1.532(9)	C42 - C43	1.513(9)
C33 - C34	1.50(1)	C43 - C44	1.58(1)
C34 - C35	1.627(9)	C44 - C45	1.51(1)
O1 - C1 - Rh1	176.7(7)	O3 - C3 - Rh2	178.0(8)
O2 - C2 - Rh1	179.2(7)	O4 - C4 - Rh2	176.4(8)
C2 - Rh1 - C1	85.8(3)	C4 - Rh2 - C3	86.8(4)
C2 - Rh1 - N2	97.9(3)	C4 - Rh2 - N4	98.1(3)
N2 - Rh1 - N1	78.2(2)	N3 - Rh2 - N4	77.3(2)
C1 - Rh1 - N1	98.1(3)	C3 - Rh2 - N3	98.0(3)
C11 - N1 - C31	120.3(5)	C21 - N3 - C35	122.3(5)
C11 - N1 - Rh1	116.0(4)	C21 - N3 - Rh2	117.1(4)
C31 - N1 - Rh1	123.6(4)	C35 - N3 - Rh2	120.4(4)
C17 - N2 - C41	119.5(5)	C27 - N4 - C45	122.5(6)
C17 - N2 - Rh1	117.1(4)	C27 - N4 - Rh2	116.7(4)
C41 - N2 - Rh1	123.4(4)	C45 - N4 - Rh2	120.8(4)
N1 - C11 - C12	120.4(6)	N3 - C21 - C22	118.8(6)
N1 - C11 - C17	114.4(5)	N3 - C21 - C27	112.6(5)
C12 - C11 - C17	125.1(6)	C22 - C21 - C27	128.7(7)
C13 - C12 - C11	130.2(7)	C23 - C22 - C21	131.6(7)
C12 - C13 - C14	131.0(8)	C24 - C23 - C22	128.3(7)
C15 - C14 - C13	127.0(8)	C23 - C24 - C25	125.9(7)
C16 - C15 - C14	129.2(8)	C26 - C25 - C24	129.3(7)
C15 - C16 - C17	132.4(4)	C25 - C26 - C27	129.7(7)
N2 - C17 - C16	121.9(6)	N4 - C27 - C26	118.5(6)
N2 - C17 - C11	113.8(5)	N4 - C27 - C21	116.0(6)
C16 - C17 - C11	124.3(6)	C26 - C27 - C21	125.5(7)
N1 - C31 - C32	113.7(5)	N2 - C41 - C42	111.7(5)
C31 - C32 - C33	112.8(5)	C41 - C42 - C43	110.9(5)
C32 - C33 - C34	111.3(5)	C44 - C43 - C42	111.6(6)
C35 - C34 - C33	112.7(5)	C43 - C44 - C45	113.5(6)
N3 - C35 - C34	109.8(5)	N4 - C45 - C44	112.6(6)

[a] Numbers in parentheses are errors in the last significant digit(s). See Figure 2 for atom-labeling scheme.

Table V. Final Positional Parameters for *syn*-[$Rh_2(CO)_4$(TC-5,5)] (*syn*-**1**)[a]

ATOM	X	Y	Z	Bequiv
Rh1	0.89437(3)	0.00000	0.04848(3)	3.38(1)
Rh2	0.61714(3)	0.00000	0.15579(3)	4.51(3)
O1	0.8077(3)	0.1241(2)	-0.1173(3)	8.2(2)
O2	0.6079(3)	0.1239(3)	-0.0387(3)	9.0(2)
N1	0.9552(2)	0.07740(17)	0.1696(3)	3.8(1)
N2	0.6212(2)	0.07741(18)	0.2960(3)	4.0(1)
C1	0.8406(3)	0.0765(3)	-0.0537(4)	5.2(2)
C2	0.6121(3)	0.0767(4)	0.0351(4)	6.3(2)
C11	1.0071(2)	0.0444(2)	0.2596(3)	4.4(2)
C12	1.0579(3)	0.0933(4)	0.3437(4)	7.1(3)
C13	1.1147(4)	0.0742(7)	0.4423(5)	11.1(5)
C14	1.1432(7)	0.00000	0.4905(10)	10.7(8)
C21	0.6216(2)	0.0447(2)	0.4055(3)	3.6(1)
C22	0.6218(3)	0.0924(2)	0.5086(4)	5.0(2)
C23	0.6229(4)	0.0737(3)	0.6258(4)	6.1(2)
C24	0.6232(5)	0.00000	0.6819(6)	6.1(4)
C31	0.9460(3)	0.1665(2)	0.1599(4)	5.3(2)
C32	0.8797(3)	0.2014(2)	0.2426(4)	5.9(2)
C33	0.7850(3)	0.1702(2)	0.2192(4)	5.1(2)
C34	0.7194(3)	0.2010(2)	0.3054(4)	5.0(2)
C35	0.6249(3)	0.1663(2)	0.2825(4)	5.2(2)

[a] Numbers in parentheses are errors in the last significant digit(s). See Figure 4 for atom-labeling scheme.

Table VI. Interatomic Distances (Å) and Angles (deg) for *syn*-[$Rh_2(CO)_2$(TC-5,5)] (*syn*-**1**)[a]

Rh1 —— Rh2	4.392(4)		
Rh1 - C1	1.842(5)	Rh2 - C2	1.854(5)
Rh1 - N1	2.022(3)	Rh2 - N2	2.028(3)
N1 - C11	1.335(5)	N2 - C21	1.347(5)
N1 - C31	1.477(5)	N2 - C35	1.474(5)
C1 - O1	1.143(6)	C2 - O2	1.136(7)
C11 - C11′	1.462(8)	C21 - C21′	1.472(7)
C11 - C12	1.411(6)	C21 - C22	1.403(5)
C12 - C13	1.372(8)	C22 - C23	1.356(6)
C13 - C14	1.39(1)	C23 - C24	1.369(6)
C31 - C32	1.526(7)	C32 - C33	1.499(6)
C33 - C34	1.522(7)	C34 - C35	1.516(6)
O1 - C1 - Rh1	179.7(5)	O2 - C2 - Rh2	179.2(5)
C1 - Rh1 - N1	97.7(2)	C2 - Rh2 - N2	98.1(2)
N1 - Rh1 - N1′	78.1(2)	N2 - Rh2 - N2	77.9(2)
C11 - N1 - C31	120.3(3)	C21 - N2 - C35	119.7(3)
C11 - N1 - Rh1	116.8(3)	C21 - N2 - Rh2	117.5(2)
C31 - N1 - Rh1	122.9(2)	C35 - N2 - Rh2	122.9(2)
N1 - C11 - C12	121.2(4)	N2 - C21 - C22	122.4(3)
N1 - C11 - C11′	114.0(2)	N2 - C21 - C21′	113.6(2)
C12 - C11 - C11′	124.8(3)	C22 - C21 - C21′	124.1(2)
C13 - C12 - C11	131.9(7)	C23 - C22 - C21	132.8(4)
C12 - C13 - C14	131.6(9)	C24 - C23 - C22	130.7(5)
C13 - C14 - C13′	123.0(10)	C23 - C24 - C23′	124.9(6)
N1 - C31 - C32	112.9(3)	C35 - C34 - C33	113.6(3)
C31 - C32 - C33	114.1(4)	N2 - C35 - C34	113.5(3)
C32 - C33 - C34	114.6(4)		

[a] Numbers in parentheses are errors in the last significant digit(s). See Figure 4 for atom-labeling scheme.

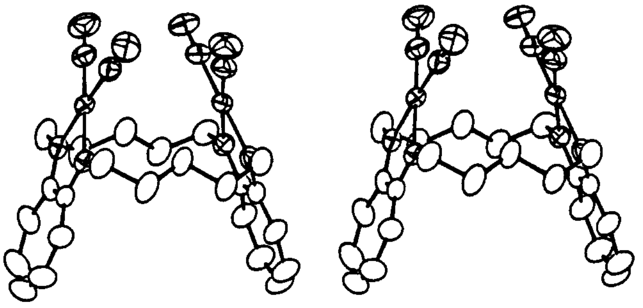

Figure 5. Stereoview of the structure of *syn*-**1**.

and two terminally bound molecules of CO comprising the coordination spheres. The metal–metal separation in the anti compound is 5.892 (1) Å while, in the syn isomer, it is 4.392 (4) Å. The average Rh–C, Rh–N, and C–O bond lengths are identical for the two isomers (Tables IV and VI). The largest structural difference occurs in the imino (C=N) bond lengths, 1.368 (10) Å for *anti*-**1** and 1.341 (7) Å for *syn*-**1**, and is statistically insignificant. The average N–Rh–N bite angles are small and nearly identical (anti = 77.8 (3)° and syn = 78.0 (3)°). The Rh–C–O bond angles are nearly linear. The two rhodium atoms and the aminotroponeiminate ring carbon atoms, labeled C14 and C24 in the *syn*-**1** structure, lie in a crystallographically imposed mirror plane that relates the halves of the molecule (Figure 4).

Temperature-Dependent Nuclear Magnetic Resonance Studies. In order to determine whether the syn and anti isomers of **1** could be thermally interconverted, pure samples were sealed under vacuum in chloroform-d_1/benzene-d_6 solvent mixtures and heated above room temperature (50–80 °C). Mixtures of the two stereoisomers were obtained along with some dark precipitate, possibly a decomposition product. The relative amounts of the two compounds depend on temperature, with syn:anti ratios of 1.92 and 1.43 occurring after the pure syn isomer was heated at 47 °C for 1 week or at 80 °C for 3 h, respectively. At 130 °C (*o*-xylene-d_{10}), the ratio was 1.07. The frequency difference ($\Delta\nu$) between resonances labeled A (unique to *syn*-**1**) and B (unique to *anti*-**1**) decreases from 81.0 Hz at 19 °C to 55.6 Hz at 130 °C, reflecting a temperature dependence of their chemical shifts (Figure 6). Also apparent from Figure 6 is the disappearance at 130 °C of the multiplet at δ 2.44, unique to *syn*-**1**. This feature, which is still present at 80 °C, reappears upon cooling.

An estimate for the lower limit on the rate of syn/anti interconversion can be obtained from coalescence eq 1, where $\Delta\nu$ =

$$k = \frac{\pi(\Delta\nu)}{2^{1/2}} = 124\ \mathrm{s}^{-1} \qquad (1)$$

($\nu_A - \nu_B$), the difference in frequency (Hz) of resonances A and B, is 55.6 Hz, and k is the rate constant. With a value for T of 403 K (130 °C) in the Eyring equation[16] (eq 2), the lower limit

$$\Delta G^{\ddagger} = -RT[\ln(k/T) + \ln(h/\beta)] \qquad (2)$$

for the free energy of activation, $\Delta G^{\ddagger}$, can be estimated to be 20

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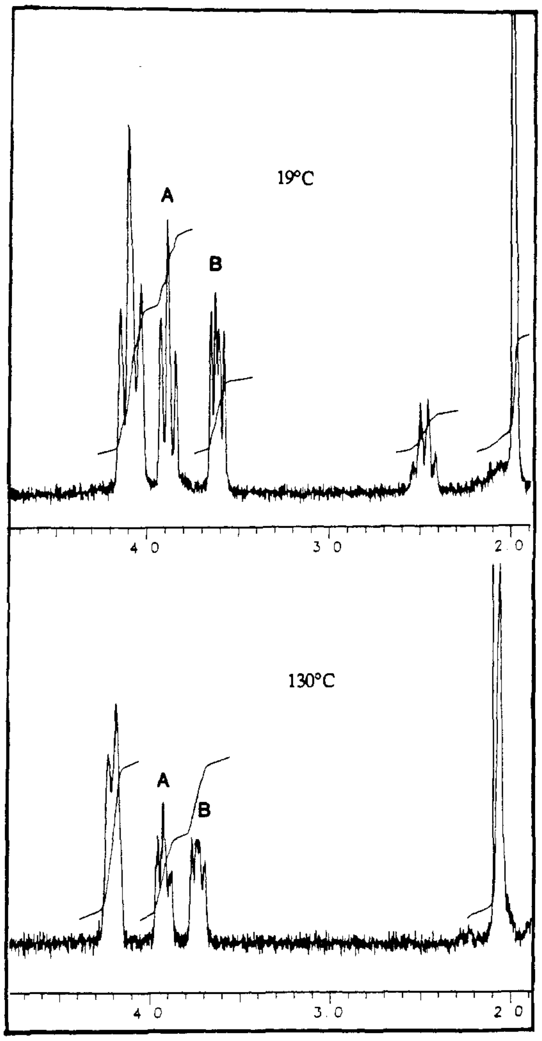


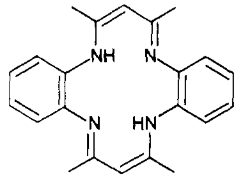
Figure 6. Portion of the 300-MHz proton NMR spectrum of a mixture of *syn*-**1** and *anti*-**1** recorded at 19 (top) and 130 °C (bottom). The large resonance at $\sim\delta$ 2.0 in both spectra is due to residual protons in the *o*-xylene-d_{10} solvent.

kcal/mol. Since it is clear from Figure 6 that 130 °C is well below the coalescence temperature, the actual value for $\Delta G^\ddagger$ is probably much higher.

Discussion

Previous studies had shown that tropocoronands, H_2(TC-n,n'), can adopt various conformations as a function of n,n' for both mononuclear and binuclear transition-metal complexes. In the case of bimetallic compounds, an S-shaped or "staircase" geometry was found for [$Cu_2(CO)_2$(TC-5,5)],[6] while a "saddle-shaped" arrangement of the ligand was observed in compounds where an exogenous bridging ligand connects the metal atoms.[4,5] The polymethylene linker chains and the two metal-binding poles of the tropocoronands comprise the macrocyclic ring, the conformational preferences of which determine whether the metal atoms of a dinuclear complex will lie on opposite sides of the ligand mean plane or on a common face. The latter conformation is of greater interest with respect to bimetallic activation of substrate molecules. The synthesis and purification of the two stereoisomers of [$Rh_2(CO)_4$(TC-5,5)], *anti*-**1** and *syn*-**1**, allow investigation of the isomerization process and measurement of the physical and spectroscopic properties unique to each isomer.

The molecular structures of the anti and syn isomers of **1** are shown in Figures 2–5. Stereoisomerism results from the macrocyclic ring conformation which in the anti form (Figure 3) resembles a staircase, with the aminotroponeiminate rings being the steps and the linker chains the risers, but is saddle-shaped in *syn*-**1** (Figure 5). Of the few known dirhodium(I) tetracarbonyl compounds with N-donor ligands,[15,17] only two others have been characterized structurally, namely [$Rh_2(CO)_4$(TMTAA)] (**2**), where (TMTAA)H_2 = 5,7,12,14-tetramethyldibenzo[*b*,*i*]-1,4,8,11-tetraaza[14]annulene,[18] and [$Rh_2(CO)_4$(OEP)] (**3**), where OEP = octaethylporphyrin.[19] In these molecules, the $\{Rh(CO)_2\}$ moieties are held exclusively in either syn (**2**, Rh$\cdots$Rh = 3.086 Å) or anti (**3**, Rh$\cdots$Rh = 3.094 Å) positions. The Rh–CO bond lengths are comparable in the four compounds ($\sim$1.85 Å), although the Rh–N distances are longer in **2** (2.071 (4) Å) and **3** (2.082 (11) Å) than in *syn*-**1** and *anti*-**1** (2.025 (5) Å). In the case of **3**, the rigid porphyrin ring is unable to accommodate the saddle-shaped geometry required to place both rhodium atoms on the same ligand face, as occurs in **2** and *syn*-**1**. The reason why the anti form of **2** does not exist is less obvious, since there is no apparent restriction on which direction the annulene portions of the ligand can twist away from the plane of the aromatic rings. The fact that both isomers are obtained with the tropocoronands is consistent with the greater flexibility of the saturated polymethylene linker chains. Two tricarbonyl-bridged dirhodium(I) complexes of binucleating macrocycles have been described,[20] but these differ significantly from the $\{Rh_2(CO)_4\}$-containing class.



(TMTAA)H_2

The rhodium dicarbonyl tropocoronand complexes are thermally stable. Solid samples heated to 200 °C showed only a small decrease in the intensity of the CO absorption band in the infrared spectrum. This stability facilitated the high-temperature NMR solution study, during which only a small amount of decomposition was observed. Resonances A and B, corresponding to the resolved α-CH_2 protons in the two isomers, do not coalesce even at 130 °C (Figure 6). Apparently, tropocoronand ring inversion in the presence of the coordinated $\{Rh(CO)_2\}$ moieties has a high energy barrier, in excess of 20 kcal/mol. Examination of a tabulation[21] of conformational barriers for inverting organic rings with greater than eight members reveals several $\Delta G^\ddagger$ values in excess of 20 kcal/mol. The steric bulk of the $\{Rh(CO)_2\}$ "substituents" in the 16-membered ring of **1** would contribute to a high conformational barrier to ring inversion. Interconversion of **1** does occur above room temperature on the chemical time scale, however, and any reaction carried out at elevated temperatures would contain both isomers.

Figure 6 also indicates that the multiplet at δ 2.44 in the spectrum of *syn*-**1** disappears at 130 °C. We have assigned this resonance to the two protons attached to the middle carbons (C33, Figure 4) of the pentamethylene linker chains (one proton for each carbon), which are pointed toward the interior of the macrocyclic cavity and, hence, are closer to the rhodium atoms (Rh$\cdots H_A$ = 3.184 Å) than their geminal partners directed toward the outside of the ring (Rh$\cdots H_B$ = 3.826 Å). Conversely, the latter protons are closer to the oxygen atoms (O$\cdots H_B$ = 3.178 Å) than the former ones (O$\cdots H_A$ = 3.815 Å). The metal-proton interaction is probably responsible for the deshielding effect, since the related compound [Cu_2(μ-PhC$\equiv$CPh)(TC-5,5)] exhibits a similar

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downfield resonance at δ 2.42.[22] At 130 °C, there is presumably considerable conformational motion in the linker chain, such that the special metal–proton shielding interaction is averaged out. The integrated intensity of the broad upfield resonances (δ 1.61–1.32) corresponding to the remaining protons of the linker chain increases by the required amount at this higher temperature, indicating that protons (H_A) now resonate at a more normal frequency. The signals due to the geminal partners (H_B) are obscured in the upfield region of the proton spectrum at room temperature, preventing determination of the free energy of activation for this linker chain conformational rotation phenomenon.

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Registry No. *anti*-**1**, 111410-36-7; *syn*-**1**, 111467-16-4; $[Rh(CO)_2Cl]_2$, 14523-22-9.

Supplementary Material Available: Tables reporting heavy-atom thermal parameters (Tables S1 and S4) and hydrogen atom parameters (Tables S2 and S5) for *syn*-**1** and *anti*-**1** (4 pages); tables of observed and calculated structure factors (Tables S3 and S6) for *syn*-**1** and *anti*-**1** (25 pages). Ordering information is given on any current masthead page.

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[22] Villacorta, G. M.; Whang, E.; Lippard, S. J., unpublished results.

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Synthesis, Structure, and Characterization of the Tetranuclear Iron(III) Oxo Complex $[Fe_4O_2(BICOH)_2(BICO)_2(O_2CPh)_4]Cl_2$

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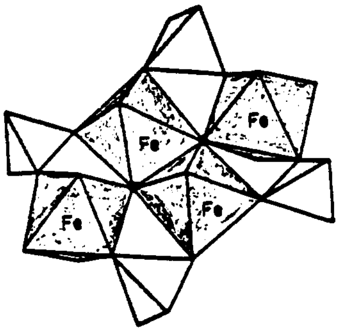
Received August 31, 1987

The synthesis and characterization of a novel molecule containing the bis(μ_3-oxo)tetrairon(III) core, $[Fe_4O_2(BICOH)_2(BICO)_2(O_2CPh)_4]Cl_2$, where BICOH is bis(*N*-methylimidazol-2-yl)carbinol, are reported. Structural, magnetic, and Mössbauer studies indicate the presence of antiferromagnetically coupled iron(III) ions with a diamagnetic ground state. The $\{Fe_4O_2\}^{8+}$ core is formally comprised of two (μ-oxo)bis(μ-benzoato)diiron(III) centers, of the kind present in the marine invertebrate respiratory protein hemerythrin, joined by linkages between oxo ligands and iron atoms of the $\{Fe_2O\}^{4+}$ constituents. Additional bridges between the two $\{Fe_2O\}^{4+}$ components are provided by the $BICO^-$ ligands. The resulting tetranuclear complex has a planar Fe_2O_2 "kernel" with Fe–O bond lengths of 1.94 (1) and 1.98 (1) Å, Fe–O–Fe angles of 95.7 (5)°, and O–Fe–O angles of 84.3 (5)°. Within the $\{Fe_2O(O_2CPh)_2\}^{2+}$ subfragment the Fe–O bond lengths are 1.884 (9) Å and, shared with the kernel, 1.94 (1) Å, while the Fe–O–Fe angle is 119.0 (6)°. Similar $\{Fe_4O_2\}$ tetranuclear cores occur in the minerals amarantite and leucophosphite, as well as the recently reported discrete complex $[Fe_4O_2(O_2CCF_3)_8(H_2O)_6]$, the geometric properties of which are compared and analyzed. Optical spectroscopic features at ~465–475 and 565–575 nm are suggested to be characteristic of the $\{Fe_4O_2\}^{8+}$ unit. The coordinating properties of the biologically relevant bidentate BICOH ligand and its deprotonated, tridentate bridging $BICO^-$ derivative are described. X-ray studies were carried out on $[Fe_4O_2(BICOH)_2(BICO)_2(O_2CPh)_4]Cl_2\cdot 5H_2O\cdot 2CH_3CN$, which crystallizes in the trigonal system, space group $R\bar{3}$, with $a = b = 39.128$ (8) Å, $c = 17.833$ (7) Å, $V = 23\,644$ Å^3, $Z = 9$, and $\rho_{calcd} = 1.106$ g cm^{-3}.

Introduction

Polynuclear oxo- or hydroxo-bridged iron(III) centers occur in a variety of proteins. Hemerythrin (Hr),[1] ribonucleotide reductase (RR)[2] and, probably, purple acid phosphatases (PAP)[3] contain binuclear units, while ferritins (Ft) and hemosiderins (Hs) have polynuclear units of uncertain size.[4] Planar tetranuclear oxo- and hydroxo-bridged iron(III) clusters also occur in nature in at least two minerals, amarantite, $[Fe_4O_2(SO_4)_4]\cdot 14H_2O$,[5] and leucophosphite, $K_2[Fe_4(OH)_2(PO_4)_4(H_2O)_2]\cdot 2H_2O$.[6] The FeO_6 octahedra in these minerals are arranged at the corners of a rhombus



where the sulfate and phosphate anions are represented by tetrahedra. In leucophosphite there are two μ_3-OH units bridging the four iron atoms, while in amarantite their place is taken by two μ_3-oxo units. Both structures are polymeric.

Apart from the tetranuclear iron(III) complex (**1**) that forms the basis for this report, several related compounds have recently been synthesized. These include $[Fe_4O_2(O_2CCF_3)_8(H_2O)_6]\cdot 2H_2O$ (**2**),[7] $(Et_4N)[Fe_4O_2(O_2CPh)_7(H_2B(pz)_2)_2]$ (**3**),[8] where $H_2B(pz)_2^-$ is the dihydrobis(1-pyrazolyl)borate anion, $Na_6[Fe_4L_2O_2(CO_3)_2]$ (**4**),[9] where L is the pentaanionic form of [(2-hydroxy-1,3-

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