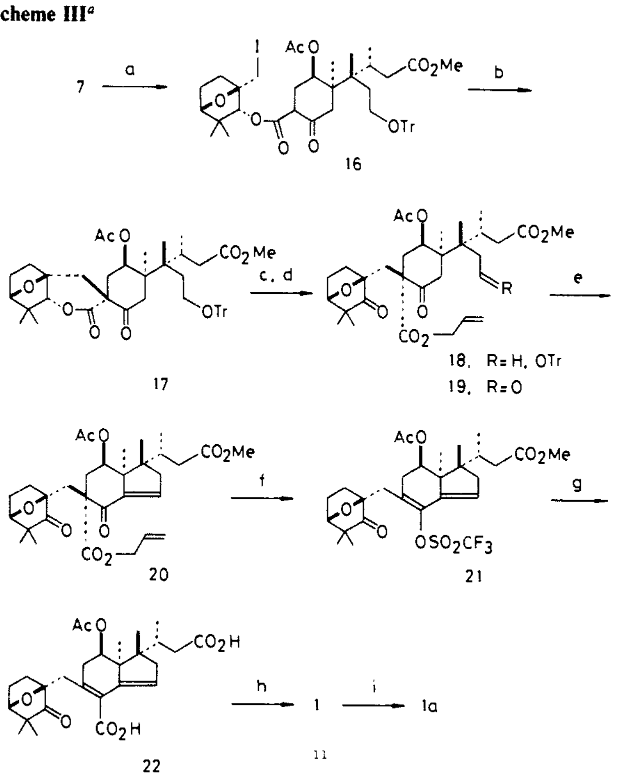
Scheme III[a]



[a] Reagents: (a) bromomagnesium thioureide–CO_2 complex, DMF, 20 °C, 20 h: **6**, DCC, DMAP, CH_2Cl_2, 0 → 20 °C, 20 h (84% "90%"); (b) KF (3 equiv), 18-crown-6-ether (3 equiv), MeCN; 65 °C, 15 h (76% "94%"); (c) sodium allyloxide; Swern oxidation (73% "90%"); (d) PTS; Swern oxidation (91%); (e) *t*-BuOK, DME, −78 °C; 2-$FC_5H_4NMe\cdot OTs$, Et_3N, CH_2Cl_2 (54%); (f) $Pd(OAc)_2$, $(C_6H_5)_3P$, HCO_2H, Et_3N, THF; $(CF_3SO_2)_2NC_6H_5$, NaH (76%); (g) CO, Bu_3N, $Pd(OAc)_2$, DPPF, aqueous DMF, 95 °C, 3.5 h; (h) NaOMe (66%); (i) *p*-$BrC_6H_4COCH_2Br$, $(i\text{-}Pr)_2NEt$, MeCN (99%).

After many fruitless attempts, we hoped to submit these compounds to an *intramolecular* coupling. Thus, (Scheme III) treatment of the compound **7** with the bromomagnesium thioureide–carbon dioxide complex,[12] resulted in α-carboxylation to yield β-ketocarboxylic acid, which was immediately reacted with **6** in the presence of dicyclohexylcarbodiimide to afford β-keto ester **16**. Further reaction of **16** with potassium fluoride in MeCN in the presence of 18-crown-6 at 65 °C effected the relevant coupling between C(9) and C(19), giving δ-lactone **17** in high yield.[13] The lactone **17**, when treated with sodium allyloxide and then oxidized,[14] was transformed into β-keto ester **18**, which was submitted to detritylation with acid and subsequent oxidation[14] to afford aldehyde ketone **19**. Treatment of **19** with potassium *tert*-butoxide in dimethoxyethane gave rise to the corresponding aldol, which was immediately dehydrated with 2-fluoropyridinium tosylate[15] to afford methoxycarbonyl enone **20**. The allyloxycarbonyl group of **20** was then removed according to the procedure of Tsuji,[16] giving the relevant dienol,[17] which was treated with sodium hydride and phenyl triflimide[18] to yield the corresponding dienyl triflate **21** in a high overall yield.

The stage was now set to introduce the necessary one-carbon unit at the C(8) position of **21**. This was accomplished by a modification of the Ortar method.[19] The compound **21**, when treated with tributylamine, palladium acetate, and 1,1′-bis(diphenylphosphino)ferrocene,[20] in aqueous *N,N*-dimethylformamide under a carbon monoxide balloon at 95 °C for 3.5 h, was transformed into acetoxyl dicarboxylic acid **22** in 42% (82% based on the recovered **21**).[21] Compound **22** was smoothly saponified and esterified to give the corresponding bis(*p*-bromophenacyl) ester alcohol. The ester thus obtained was identical in every respect (^1H NMR, IR, MS, CD, HPLC) with **1a**[1,2] derived from the natural sample. The hatch-stimulating activity of the synthetic sample **1** was found to be indistinguishable from that of the natural sample.[22]

Supplementary Material Available: Spectral data and physical properties for compounds **4–7**, **9–12**, **11a**, **14–18**, **20–22**, and an ester of **22** and listings of atomic coordinates and thermal parameters for **11** (8 pages). Ordering information is given on any current masthead page.

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(21) There is no experimental evidence available to detail how the compound **22** was produced under these conditions.

(22) Studies on the biological activity were carried out by Dr. A. Fukuzawa, Hokkaido University.

Heterobimetallic Complexes with (μ-Phenoxo)bis(μ-carboxylato) Cores

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Binuclear metal complexes are important in investigating the magnetic and electronic interactions between metal ions and in probing the structure and function of binuclear metal centers in proteins.[1,2] In studying the coordination chemistry of binucleating ligands such as *N,N′*-(2-hydroxy-5-methyl-1,3-xylene)bis(*N*-carboxymethylglycine) (HXTA) and 2,6-bis[(bis(2-pyridylmethyl)amino)methyl)]-4-methylphenol (HBPMP),[4] we have discovered a general synthetic route for preparing heterobimetallic complexes in which one of the metal ions is iron. Herein we report the synthesis and physical properties of the bis(carboxylato) bridged Fe(III)Zn(II), Fe(III)Mn(II), Fe(III)Cu(II), Ga(III)-Fe(II), and Fe(III)Fe(II) complexes of HBPMP.

The Fe(III)Zn(II) complexes were synthesized by treating a methanolic solution of HBPMP with sequential additions of an equivalent of $Fe(NO_3)_3{\cdot}9H_2O$, an equivalent of $ZnBr_2$, and 3 equiv of the appropriate carboxylate salt. The complexes were metathesized with excess $NaBPh_4$ and recrystallized from ace-

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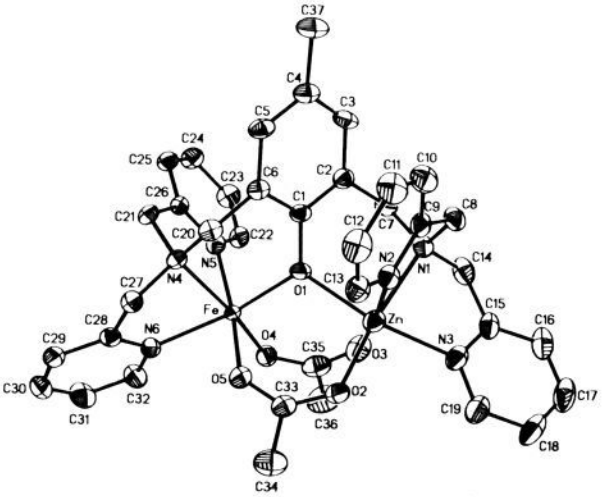

Figure 1. Plot of the structure of $[FeZnBPMP(OAc)_2]^{2+}$, showing 50% probability ellipsoids. Representative distances (Å) are as follows: Fe–O1, 1.982 (3); Zn–O1, 2.067 (3); Fe–O4, 1.939 (3); Zn–O3, 2.086 (3); Fe–O5, 2.055 (3); Zn–O2, 1.999 (3); Fe–N4, 2.193 (4); Zn–N1, 2.184 (3); Fe–N5, 2.118 (3); Zn–N2, 2.138 (3); Fe–N6, 2.146 (3); Zn–N3, 2.106 (4); Fe–Zn, 3.437 (1). Angle Fe–O1–Zn, 116.1 (1)°.

tone/methanol. The other heterobimetallic complexes were synthesized by a similar protocol, with all the complexes having satisfactory elemental analyses consistent with the formulation, $[MM'BPMP(O_2CR)_2](BPh_4)_2$.[5] The Fe(II)Fe(III) complexes were also prepared in a similar manner except that 2 equiv of $Fe(NO_3)_3{\cdot}9H_2O$ were used.[6]

The X-ray crystal structure of $[FeZnBPMP(OAc)_2](BPh_4)_2{\cdot}CH_3CN$ (**1**) (cation shown in Figure 1) clearly illustrates the binuclear nature of these complexes.[7] The metal centers are bridged by the phenolate oxygen atom of $BPMP^-$ and the two acetates, constituting what increasingly appears to be a thermodynamically favored core structure. Examples of structurally characterized homobimetallic complexes with similar triply bridged cores include the hemerythrin model complexes,[8,9] $(Me_4N)[Fe_2HXTA(OAc)_2]$[3a] and $[Mn_2BPMP(OAc)_2](ClO_4)_2$.[10] In all these structures, the metal–metal distance is constrained by the carboxylate bridges to be less than 3.5 Å. The Fe–Zn distance in **1** is 3.437 (1) Å, comparable to the metal–metal separations of $[Mn_2BPMP(OAc)_2]^{2+}$ (3.447 (1) Å)[11] and $[(HBpz_3Fe)_2OH(OAc)_2]^+$ (3.439 (1) Å),[10a] which have either a phenolate and a hydroxide as the single atom bridge.

Table I. Mössbauer and Electrochemical Properties of the Heterobimetallic Complexes.

no.	complex	δ^a	%Fe	$\Delta E_Q{}^a$	$E^{\circ\prime\,b}$	$\Delta E_{pp}{}^b$
1	$[FeZnBPMP(OAc)_2](BPh_4)_2$				−4	59
2	$[FeZnBPMP(OPr)_2](BPh_4)_2$	*c*		*c*	−19	60
3	$[Fe_2BPMP(OPr)_2](BPh_4)_2$	1.13^d	50	2.69^d	−10	60
		0.48^d	50	0.50^d	692	68
4	$[Fe_2BPMP(OBz)_2](PF_6)_2$	1.16^e	50	2.40^e	60	60
		0.46^e	50	0.48^e	750	60
5	$[FeMnBPMP(OPr)_2](BPh_4)_2$	0.45	100	0.49	24	61
6	$[FeCuBPMP(OPr)_2](BPh_4)_2$	0.46	85^f	0.39	6	62
7	$[GaFeBPMP(OPr)_2](BPh_4)_2$	1.18	100	2.48	587	60

[a] Units of mm/s; isomer shifts relative to Fe metal at room temperature. [b] Units of mV versus SCE, in CH_3CN solution under N_2 at room temperature. [c] No quadrupole doublets were observed, consistent with a slow relaxing high-spin Fe(III) center. [d] CH_3CN at 55 K. [e] CH_3COCH_3 at 55 K. [f] Minority species (15%) observed with δ = 0.49 mm/s and ΔE_Q = 1.18 mm/s.

The oxidation state of the iron in these complexes is most readily established with Mössbauer spectroscopy (Table I). At 55 K, complexes **3** and **4** exhibit two quadrupole doublets of equal intensity with parameters typical of a high spin Fe(III)–high spin Fe(II) formulation.[3b] At 4.2 K the spectra of complexes display magnetic features even in zero applied magnetic field, showing that the two metal centers are spin-coupled to a state with half-integer system spin. The spectra of **2** display magnetic hyperfine interactions even at 200 K which is typical of Fe(III) with long spin relaxation time. Complexes **5** and **6** exhibit, in zero field, quadrupole doublets with parameters typical of high-spin ferric ions. The absence of magnetic hyperfine interactions at 4.2 K (in zero field) suggests that the ferric ion is coupled to Mn(II) and Cu(II), respectively, to yield complexes with integer system spin. Complex **7**, unlike the other heterobimetallic complexes, exhibits a doublet typical of high-spin Fe(II). The isolation of Fe(III)Fe(II) and Ga(III)Fe(II) complexes from a synthetic procedure that uses the trivalent ions as starting material indicates the participation of a redox process during complex formation. Insights into this process can be obtained from the cyclic voltammetric data.

The electrochemical properties of the complexes under study are found in Table I. Complex **3** exhibits redox processes at +692 and −10 mV versus SCE[11] corresponding to the one-electron oxidation and reduction of **3**, respectively. Substitution of Ga(III) for Fe(III), as in **7**, retains only the high potential wave at 587 mV versus SCE. The high potentials observed in these complexes can be used to rationalize the isolation of **3**, **4**, and **7** as opposed to their more oxidized counterparts. Substitution of Zn(II) for Fe(II), as in **2**, gives rise to a wave at −19 mV versus SCE, affording a dramatic contrast in the effects of substitution of divalent and trivalent ions. Similarly, the Fe(III)Mn(II), **5**, and Fe(III)Cu(II), **6**, complexes exhibit reversible features near 0 mV versus SCE, associated by analogy to **2**, with the reduction of Fe(III). Interestingly, no evidence for the oxidation of the Mn(II) center is observed. For comparison, $[Mn_2BPMP(OAc)_2]^{2+}$ exhibits quasi-reversible one-electron waves at 470 and 1020 mV versus SCE.[12]

We have demonstrated here a general approach for the rational synthesis of heterobimetallic complexes. The availability of these complexes opens up possibilities for investigating magnetic and electronic interactions between metal centers in a systematic way. Studies focusing on the magnetochemical, EPR, and NMR

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(5) Abbreviations: OAc, acetate; OPr, propionate; OBz, benzoate; $HBpz_3$, hydrotris(pyrazolyl)borate; $TBABF_4$, tetrabutylammonium tetrafluoroborate; SCE, standard calomel electrode.

(6) This procedure only yielded the $[Fe(II)Fe(III)BPMP(O_2CR)_2]^{2+}$ even though no ferrous precusor was employed. $[Fe_2BPMP(OBz)_2]^{2+}$ was metathesized with NH_4PF_6 and recrystallized from hot/cold methanol.

(7) The complex crystallized from an CH_3CN/CH_3COCH_3 solution (after vapor diffusion of methanol) as $[FeZnBPMP(OAc)_2](BPh_4)_2{\cdot}CH_3CN$, triclinic, $P\bar{1}$. Cell constants (146 K): $a = 12.914$ (4) Å, $b = 14.991$ (3) Å, $c = 20.736$ (6) Å, $\alpha = 101.66$ (2)°, $\beta = 106.84$ (2)°, $\gamma = 100.19$ (2)°, $Z = 2$, $V = 3642$ Å^3. With the use of 11 105 of 13 462 reflections for which I(obsd) $> 1.25\sigma(I)$ (146 K, Mo Kα (λ = 0.7107 Å) radiation, $2\theta_{max} = 50°$, Nicolet R3m diffractometer), the structure was solved by direct methods (SOLV, G. M. Sheldrick) and refined (anisotropic thermal parameters on non-H atoms) to $R = 0.070$ and $R_w = 0.095$. Bond length considerations from the assignment of the metal atom identities are shown in Figure 1. However, refinement of that model gave U_{iso} values for the Fe and Zn that differed by almost a factor of 2, suggesting some disorder involving the two metals. Switching the Fe and Zn atoms gave R and R_w values approximately 0.01 higher than those for the original assignment. Calculations using the original assignments for Fe and Zn and variable site occupancy factors supported partial, but not random, disorder. Since the calculations indicated that Fe and Zn predominate at the sites shown in Figure 1, the final model incorporated fixed site occupancy factors for Fe and Zn of 1.0. While ignoring the modest degree of disorder present, this model has the advantage of eliminating reliance on simultaneous refinement of the highly correlated thermal and size occupancy parameters.

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properties of these complexes are in progress. In particular, the availability of Fe(III)Zn(II) and Ga(III)Fe(II) analogues of the Fe(III)Fe(II) complex will allow us to study in detail the electronic properties of the individual paramagnetic centers and then apply the information toward a better understanding of the spin-coupled mixed-valence Fe(III)Fe(II) complexes.

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Supplementary Material Available: Tables of atomic positional and thermal parameters for $[FeZnBPMP(OAc)_2](BPh_4)_2 \cdot CH_3CN$ (5 pages). Ordering information is given on any current masthead page.

Metazidohemerythrin Models Featuring a Bis-Benzimidazole Tripod Ligand. Structure and Spectroscopy of (μ-Oxo)bis(μ-benzoato)bis(bis(2-benzimidazolylmethyl)amine)diiron(III)†

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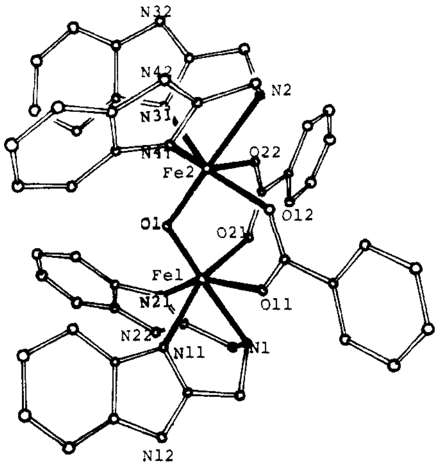
There is increasing interest in non-heme single iron and diiron proteins.[1-6] In this respect, the characterization of low molecular weight models has proved to be of crucial importance.[7-13] Hemerythrin,[1-3,4b-d] ribonucleotide reductase,[5] and several purple acid phosphatases[4a,6] are diiron proteins that in their fully oxidized forms contain the Fe(III)–O–Fe(III) motif. In hemerythrin the protein also provides μ-carboxylato bridges and imidazole ligands. Several synthetic models for metazidohemerythrin have been reported recently (1,[7a] 2,[8a,b] 3[9]). These models feature amine tripod ligands,[14] in addition to oxo and carboxylato bridges.



$[N3\ Fe\ C_6H_5COO\ ]_2O\ (ClO_4)_2 \cdot 2C_2H_5OH\ .\ 0.5(Et_3NH\ ClO_4)$

Fe1-O1	1.777(5)	Fe2-O1	1.802(6)
Fe1-O11	2.047(5)	Fe2-O12	2.028(4)
Fe1-O21	2.035(5)	Fe2-O22	2.034(5)
Fe1-N1	2.284(6)	Fe2-N2	2.289(8)
Fe1-N11	2.108(7)	Fe2-N31	2.091(5)
Fe1-N21	2.131(7)	Fe2-N41	2.116(6)

Fe1..Fe2	3.079(2)
Fe1-O1-Fe2	118.7(3)

Figure 1. ORTEP diagram of 4 with selected bond distances in Å and angles in deg. Numbers in parentheses are estimated standard deviations.

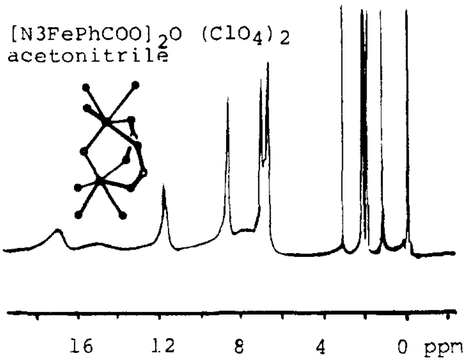


Figure 2. ^1H NMR (300 MHz) of 4 in CD_3CN. The peak at 17 ppm is the only one disappearing upon exchange with D_2O (imidazole N–H). No other peaks were observed from −20 to 100 ppm.

$$\underset{\mathbf{1}}{[HBpz_3CH_3COOFe]_2O} \qquad \underset{\mathbf{2}}{[tacnCH_3COOFe]_2O\ I_2}$$

$$\underset{\mathbf{3}}{[tpbn(CH_3COO)_2Fe_2O]_2(NO_3)_4}$$

We sought to prepare models with imidazole-based tripod ligands that would allow us to examine the N–H resonance and

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[†] Presented in part at the 194th National Meeting of the American Chemical Society, Fall 1987; Division of Inorganic Chemistry, Abstract no. 120.

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