Inorg. Chem. **1999,** *38,* 3316−3320

Bis-macrocyclic Ligands with Two Ferrocenyl End Groups, and Their Tetranuclear Dicopper(I) Compounds

Peter Comba,[*,†] Jürgen Ensling,[‡] Philipp Gütlich,[‡] Andreas Kühner,[†] Alexander Peters,[†] and Hans Pritzkow[†]

Anorganisch-Chemisches Institut, Im Neuenheimer Feld 270, 69120 Heidelberg, Germany, and
Institut für Anorganische Chemie und Analytische Chemie, Johannes Gutenberg Universität Mainz,
Staudinger Weg 9, 55099 Mainz, Germany

Received December 3, 1998

A series of bismacrocyclic ligands with two ferrocenyl groups, *exo*/*endo*-1,1′:1″,1‴-[1,2,4,5-tetrakis(5-aza-2-thiahexa-5-enyl)benzene]bisferrocene (*exo*/*endo*-FeBeFe), 1,1′:1″,1‴-[1,2:1′,2′-tetrakis(5-aza-2-thiahexa-5-enyl)ethene]bisferrocene (1,2-FeEnFe), 1,1′:1″,1‴-[1,1′:2,2′-tetrakis(5-aza-2-thiahexa-5-enyl)ethene]bisferrocene (1,1-FeEnFe), 1,1′:1″,1‴-[tetrakis(5-aza-2-thiahexa-5-enyl)methane]bisferrocene (FeMeFe), and their dicopper(I) compounds have been synthesized and characterized (electrochemistry, IR, NMR and Mössbauer spectroscopy). The molecular structure of *endo*-FeBeFe has been determined by X-ray structure analysis and the copper(I)-induced discrimination of the *exo*- and *endo*-isomers of FeBeFe has been investigated by ^{1}H NMR spectroscopy. The interaction between copper and iron in the tetranuclear compounds is discussed on the basis of the electrochemical and spectroscopic data.

Introduction

There is a strong interest in the design and synthesis of macrocyclic and macrobicyclic ligands with redox centers in close proximity to a cation or anion binding site.[1] It has been suggested that such systems may induce intermetallic energy-transfer or electron-transfer processes[2] or act as versatile electron reservoir systems.[2,3] Oligonuclear compounds with redox centers close to crown ether derivatives have also been used as molecular switching devices.[4] Probably the most widely used redox-active group with a reversible single-electron process is ferrocene. Among ligand systems bearing ferrocenyl end-groups there is the prominent group of ferrocenyl polyaza macrocyclic compounds, obtained by reduction of the corresponding Schiff-base products with $NaBH_4$.[5]

As an extension to our previous work on transition metal compounds of 30−36-membered macrocyclic Schiff-base ligands with N_2S_2 donor sets,[6] we now report the syntheses of a series of bismacrocylic systems with two ferrocenyl end-groups and two cavities with mixed imine thia donor sets. These bismacrocyclic ligands are well suited for copper(I) coordination chemistry, leading to heterotetranuclear Cu_2Fe_2 compounds. There is a variety of reactions that yields ligands with ferrocenyl groups in the backbone. Schiff-base ligands with ferrocenyl groups have been obtained by reaction of ferrocenylamine with an appropriate aldehyde[7] or with ferrocenecarboxaldehyde and appropriate amines.[8] The stability of the resulting imines toward hydrolysis is a problem but the reduction to the corresponding amines limits their complexation with soft metal ions.

Experimental Section

Materials. 1,1′-Bisformylferrocene,[9] tetrakis[2-aminoethylsulfanylmethyl]methane,[10] and $[Cu(CH_3CN)_4]ClO_4$[11] were prepared as described before. 2-Aminoethanthiol hydrochloride was purchased from Aldrich.

Measurements. ^{1}H and ^{13}C NMR spectra, at 200.13 and 50.54 MHz, were measured with a Bruker AS 200 spectrometer in $CDCl_3$ or CD_3CN with TMS as internal standard. Infrared spectra (KBr disks)

---

[*] Corresponding author. Tel.: +49 (6221) 54 8453. Fax: +49 (6221) 54 6617. E-mail: comba@akcomba.oci.uni-heidelberg.de.

[†] Anorganisch-Chemisches Institut.

[‡] Johannes Gutenberg Universität Mainz.

(1) Beer, P. D. *Chem. Soc. Rev.* **1989**, *18*, 409.

(2) (a) Astruc, D. *New. J. Chem.* **1992**, *16*, 305. (b) Harvey, P. D.; Gan, L. *Inorg. Chem.* **1991**, *30*, 3239.

(3) (a) Astruc, D.; Hamon, J. R.; Althoff, G.; Román, E.; Batail, P.; Michand, P.; Mariot, J. P.; Varret, F.; Cozak, D. *J. Am. Chem. Soc.* **1979**, *101*, 5445. (b) Andrieux, C. P.; Blocman, C.; Dumas-Bouchiat, J. M.; M'Halla, F.; Savéant, J. M. *J. Am. Chem. Soc.* **1980**, *102*, 3806. (c) Andrieux, C. P.; Blocman, C.; Dumas-Bouchiat, J. M.; Savéant J. M. *J. Am. Chem. Soc.* **1979**, *101*, 3431. (d) Guerchais, V.; Román, E.; Astruc, D. *Organometallics* **1986**, *5*, 2505. (e) Astruc, D.; Desbois, M.-H.; Lacoste, M.; Moulines, F.; Hamon, J. R.; Varret, F. *Polyhedron* **1990**, *9*, 2727.

(4) Aberle, C.; Plenio, H. *Angew. Chem.* **1998**, *110*, 1467.

(5) (a) Beer, P. D.; Cheng, Z.; Drew, M. G. B.; Kingston, J.; Ogden, M.; Spencer, P. *J. Chem. Soc., Chem. Commun.* **1993**, 1046. (b) Beer, P. D.; Chen, Z.; Drew, M. G. B.; Johnson, A. O. M.; Smith D. K.; Spencer, P. *Inorg. Chim. Acta* **1996**, *246*, 143. (c) Tendro, M. J. L.; Benito, A.; Martínez-Máñez, R.; Soto, J. *J. Chem. Soc., Dalton Trans.* **1996**, 4121. (d) Holwerda, R. A.. T.; Robison, W.; Bartsch, R. A. *Organometallics* **1991**, *10*, 2652.

(6) (a) Comba, P.; Fath, A.; Hambley, T. W.; Richens, D. T. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1883. (b) Comba, P.; Fath, A.; Huttner, G.; Zsolnai, L. *J. Chem. Soc., Chem. Commun.* **1996**, 1885. (c) Comba, P.; Fath, A.; Hambley, T. W.; Vielfort, A. *J. Chem. Soc., Dalton Trans.* **1997**, 1691. (d) Comba, P.; Fath, A.; Hambley, T. W.; Kühner, A.; Richens, D. T.; Vielfort, A. *Inorg. Chem.* **1992**, *31*, 4389. (e) Comba, P.; Kühner, A. *Eur. J. Inorg. Chem.* **1999**, 509. (f) Comba, P.; Kühner, A.; Peters, A. *J. Chem. Soc., Dalton Trans.* **1999**, 509.

(7) (a) Bracci, M.; Ercolani, C.; Floris, B.; Bassetti, M.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Dalton Trans.* **1990**, 1357. (b) Chambron, J. C.; Coudret, C.; Sauvage, J. P. *New J. Chem.* **1992**, *16*, 361.

(8) Neuse, E. W.; Meirim, M. G.; Blom, N. F. *Organometallics* **1988**, *7*, 2562.

(9) Balavoine, G. G. A.; Doisneau, G.; Fillebeen-Khan, T. *J. Organomet. Chem.* **1991**, 381.

(10) Donlevy, T. M.; Gahan, L. R.; Hambley, T. W.; Hanson, G. R.; Markiewicz, A.; Murray, K. S.; Swann, I. L.; Pickering, S. R. *Aust. J. Chem.* **1990**, *43*, 1407.

(11) Kubas, G. J. *Inorg. Synth.* **1979**, *19*, 90.

10.1021/ic981389i CCC: $18.00

were obtained with a Perkin-Elmer 16PC FT-IR instrument, UV−vis spectra were recorded with a Cary 1E instrument, and elemental analyses were obtained from the microanalytical laboratory of the chemical institute of the University of Heidelberg. Mass spectra (EI or FAB) were measured on a Finnigan 8400 mass spectrometer. Mössbauer spectra were taken with a constant acceleration type Mössbauer spectrometer. The spectrometer was equipped with a 1024-channel analyzer, operating in the time scale mode, and a 50 mCi ^{57}Co/Rh source was employed. The isomer shifts reported are relative to α-Fe at room temperature. Spectra of the samples (thickness of about 5 mg Fe/cm) were collected at 100 K by means of a combined He continuous flow/bath cryostat. The Mössbauer spectra were analyzed with the computer program MOSFUN.[12] Cyclic voltammograms were obtained with a EG&G 273 potentiostat/galvanostat. The working electrode was a glassy disk electrode with a saturated calomel reference electrode (type Radiometer K 401). Tetrabutylammonium hexfluorophosphate and dichloromethane or acetonitrile were used as supporting electrolyte and solvent, respectively, in the electrochemical experiments. The system was calibrated against ferrocene.

Syntheses. The preparative work was carried out under argon, using standard Schlenk techniques. EtOH, THF, toluene, CH_3CN, and CH_2Cl_2 were dried by conventional methods.

1,2,4,5-Tetrakis[2-aminoethylsulfanylmethyl]benzene (1). To a solution of Na (2.04 g, 88.86 mmol) in EtOH (400 mL) was added 2-aminoethanethiol hydrochloride (5.05 g, 44.43 mmol) in one portion. After the resulting solution boiled at reflux for 1.5 h, 1,2,4,5-tetrakis-[brommethyl]benzene (5.0 g, 11.12 mmol) in EtOH/THF (1:1;150 mL) was added dropwise to the white suspension, and the resulting solution was refluxed for approximately 10 h. Cooling to room temperature, filtration, and evaporation of the solvent lead to a yellowish precipitate, which was dissolved in $CHCl_3$ (200 mL) and washed twice with water (100 mL each). The organic layer was dried with Na_2SO_4, and the solvent was removed to yield a white, waxy solid (3.9 g, 9.0 mmol, 72%). Anal. Calcd for $C_{18}H_{34}N_4S_4$: C, 49.72; H, 7.88; N, 12.88. Found: C, 49.34; H, 7.56; N, 12.21. MS (FAB): 435 (100, M$^+$). ^{1}H NMR (200.13 MHz, $CDCl_3$, δ (ppm)): 1.28 (s, NH_2); 2.53 (t, NCH_2CH_2S); 2.81 (t, NCH_2CH_2S); 3.80 (s, CH_2, benzylic); 7.11 (s, aromatic). ^{13}C NMR (50.54 MHz, $CDCl_3$, δ (ppm)): 32.8 (SCH_2, ethylene bridge); 36.2 (NCH_2, ethylene bridge); 41.0 (CH_2, benzylic); 132.7 (quaternary C); 135.3 (CH, aromatic).

Tetrakis[2-aminoethylsulfanylmethyl]ethene (2). This compound was obtained by an analogous procedure to that described in detail for **1**, resulting in a viscous, colorless oil. Yield: 3.1 g (8.3 mmol, 54%). Anal. Calcd for $C_{14}H_{32}N_4S_4$: C, 43.71; H, 8.38; N, 14.56. Found: C, 43.34; H, 8.09; N, 14.11. MS (FAB): 385 (100, M$^+$). ^{1}H NMR (200.13 MHz, $CDCl_3$, δ (ppm)): 1.56 (s, NH_2); 2.59 (t, NCH_2CH_2S); 2.86 (t, NCH_2CH_2S); 3.42 (s, CH_2). ^{13}C NMR (50.54 MHz, $CDCl_3$, δ (ppm)): 32.2 (methylene bridge), 36.5 (SCH_2, ethylene bridge); 41.5 (NCH_2, ethylene bridge); 112.3 (quaternary C).

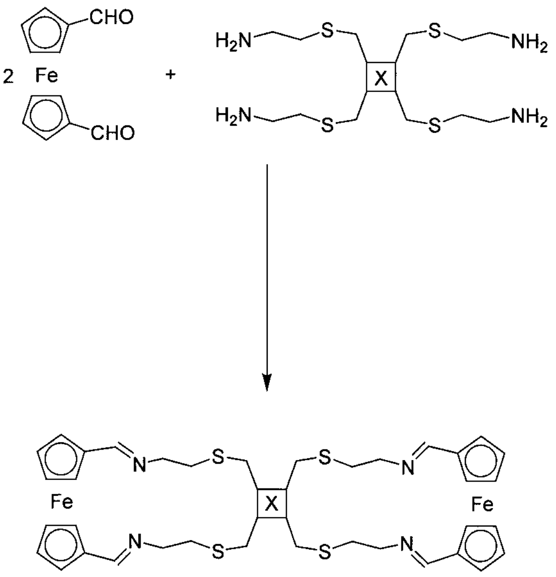
***exo*/*endo*-FeBeFe·4H$_2$O (3).** A well-stirred solution of 1,1′-bisformylferrocene (1.0 g, 4.1 mmol) and **1** (0.91 g, 2.1 mmol) in toluene (100 mL) was refluxed for 6 h. After cooling to room temperature, the resulting orange-red solution was filtered, the solvent was evaporated, and the red residue was dissolved in CH_2Cl_2 (250 mL). This was diluted with hexane (300 mL) and stored overnight at 4 °C. The resulting red crystalline product was washed with hexane and dried under vacuum. Yield: 0.88 g (1.0 mmol, 50%). Anal. Calcd for $C_{42}H_{46}N_4S_4Fe_2\cdot 4H_2O$: C, 54.90; H, 5.92; N, 6.10. Found: C, 54.96; H, 5.72; N, 6.11. IR (KBr): $\tilde{\nu}^{-1}$ [cm^{-1}] 3098 w, 1638 s, 1248 m, 1033 m, 1020 m, 811 s. UV (CH_3CN) λ_{max} nm (ϵ, M^{-1} cm^{-1}): 243−245 (3.7), 260−270 (3.7), 315−354 (0.8), 363−393 (0.3), 468−477 (0.2). MS (FAB): 847 (35, M$^+$), 372 (100, M − $C_{17}H_{20}N_2S_2Fe$). ^{1}H NMR (200.13 MHz, $CDCl_3$, δ (ppm)): 2.77 (t, NCH_2CH_2S), 3.64 (t, NCH_2CH_2S), 3.98 (s, benzylic), 4.43 (s, 3,3′-CH), 4.61 (s, 2,2′-CH), 7.01 (s, endo aromatic), 7.63 (s, exo aromatic), 8.15 (s, imine). ^{13}C NMR (50.54 MHz, $CDCl_3$, δ (ppm)): 32.7 (NCH_2CH_2S), 40.9 (benzylic), 61.2 (NCH_2CH_2S), 68.3−71.5 (2,2′ and 3,3′ aromatic), 81.7 (imine aromatic), 133.5 and 133.3 (exo and endo aromatic), 135.2 (quaternary C), 161.8 (imine).

Table 1. Experimental Data for the X-ray Diffraction Studies of *endo*-FeBeFe

empirical formula	$C_{42}H_{46}N_4S_4Fe_2$	space group	$P2_1/a$
fw	846.77 g/mol	T, °C	−70
a, Å	9.525(5)	λ, Å	0.710 73
b, Å	9.071(4)	d_x, g cm^{-3}	1.43
c, Å	22.841(11)	μ, mm^{-1}	0.99
β, deg	95.75(4)	R1^a	0.050
V, Å^3	1963.6(16)	ωR2^b	0.116
Z	2		

^{a} $R1 = \sum|F_o| - |F_c||/\sum|F_o|$. ^{b} $\omega R2 = \sqrt{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]}$.

Chart 1



X = benzene **3**, ethene **4**, spiro C **5**

1,1/1,2-FeEnFe (4). The synthesis of **4** followed essentially the same procedure as described above for **3**. Yield (orange air-sensitive powder, based on 1.0 g of 1,1′-bisformylferrocene): 0.57 g (0.7 mmol, 35%). IR (KBr): $\tilde{\nu}^{-1}$ [cm^{-1}] 3079 w, 2959 m, 1640 s, 1262 s, 1100 m, 1022 s, 810 s. UV (CH_3CN) λ_{max} nm (ϵ, M^{-1} cm^{-1}): 232 (1.9), 271 (1.2), 290−310 (0.8), 350−380 (0.2), 500−510 (0.1). MS (EI): 514 (10, M), 358 (70, M − $C_{17}H_{20}N_2S_2Fe$). ^{1}H NMR (200.13 MHz, $CDCl_3$, δ (ppm)): 2.74−2.91 (m, NCH_2CH_2S), 3.47 (s, methylene bridge), 3.54−3.75 (m, NCH_2CH_2S), 4.43 (s, 3,3′-CH), 4.68 (s, 2,2′-CH), 8.19 (s, imine). ^{13}C NMR (50.54 MHz, $CDCl_3$, δ (ppm)): 33.0 (NCH_2CH_2S), 34.1 (methylene bridge), 62.0 (NCH_2CH_2S), 69.5−71.4 (2,2′ and 3,3′ aromatic), 81.7 (imine aromatic), 116.3 (1,2:1′,2′-isomer quaternary C, 134,2 (1,1′:2,2′-isomer quaternary C), 162.0 (imine).

FeMeFe (5). Based on the method described above, the reaction of 1,1′-bisformylferrocene (0.4 g, 1.58 mmol) and tetrakis[2-aminoethylsulfanylmethyl]methane (0.30 g, 0.8 mmol) lead to a reddish orange powder. Yield: 0.25 g (0.32 mmol, 40%). IR (KBr): $\tilde{\nu}^{-1}$ [cm^{-1}] 3090 w, 1642 s, 1262 m, 1249 m, 1097 m, 1023 s, 808 s. UV (CH_3CN) λ_{max} nm (ϵ, M^{-1} cm^{-1}): 230 (2.3), 260−264 (1.6), 290−330 (0.8), 350−380 (0.2), 488−525 (0.1). MS (EI): 578 (7, M$^-$), 501 (40, M$^-$), 219 (100, M$^-$). ^{1}H NMR (200.13 MHz, $CDCl_3$, δ (ppm)): 2.83 (t, NCH_2CH_2S), 2.88 (s, methylene bridge), 3.66 (t, NCH_2CH_2S), 4.40 (s, 3,3′-CH), 4.68 (s, 2,2′-CH), 8.08 (s, imine). ^{13}C NMR (50.54 MHz, $CDCl_3$, δ (ppm)): 34.7 (methylene bridge), 39.7 (NCH_2CH_2S), 41.5 (quaternary C), 61.0 (NCH_2CH_2S), 70.3 (3,3′ aromatic), 70.6 (2,2′ aromatic), 82.8 (imine aromatic), 161.1 (imine).

[Cu$_2$(*exo*-FeBeFe)](ClO$_4$)$_2$·2H$_2$O·CH$_2$Cl$_2$ (6). A solution of **3** (1.0 g, 1.2 mmol) in toluene (50 mL) was added dropwise to a solution of $[Cu(CH_3CN)_4]ClO_4$ (0.23 g, 0.7 mmol) in acetonitrile (20 mL). After 12 h, the solvent was partly evaporated from the resulting cherry-red solution and the resulting precipitate was washed twice with dichloromethane. Yield (red-purple microcrystalline solid; recrystallized from

---

[12] Müller, W. E. MOSFUN. *Mössbauer Effect Data J.* **1981**, *4*, 89.

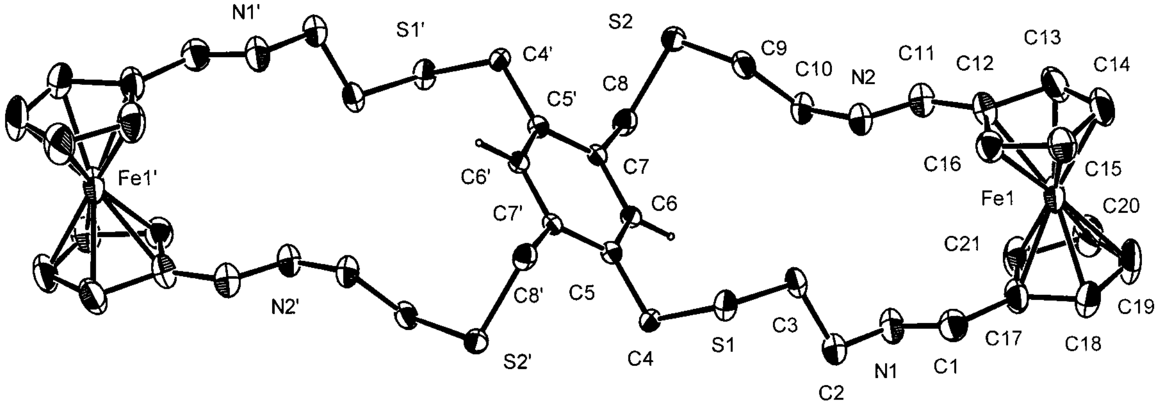


Figure 1. ORTEP drawing of the *endo*-FeBeFe complex with the atom-numbering scheme. All hydrogen atoms, except at C(6) and C(6′), are omitted for clarity.

acetonitrile): 1.05 g (0.31 mmol, 90% based on *exo*-FeBeFe). Anal. Calcd for $C_{42}H_{46}N_4S_4Fe_2Cu_2Cl_2O_8\cdot 2H_2O\cdot CH_2Cl_2$: C, 39.92; H, 4.05; N, 4.33. Found: C, 40.00; H, 3.99; N, 4.68. IR (KBr): $\tilde{\nu}^{-1}$ [cm^{-1}] 3090 w, 1620 s, 1251 m, 1070−1144 s, 830 s, 623 m. UV (CH_3CN) λ_{max} nm (ϵ, M^{-1} cm^{-1}): 233 (31.6), 258−265 (15.2), 277−288 (12.4), 319−323 (8.6), 355−380 (2.9), 465−475 (1.0). MS (FAB): 1068 (10, M − ClO_4^-), 460 (12, $C_{19}H_{20}S_2N_2CuFe$), 372 (3, $C_{14}H_{16}N_2S_3Cu$), 329 (16, $C_{13}H_{16}S_4N_2$). ^{1}H NMR (200.13 MHz, CD_3CN, δ (ppm)): 2.31−2.56 (m, NCH_2CH_2S), 3.05 (s, benzylic), 3.25−3.40 (m, NCH_2CH_2S), 5.00 (s, 3,3′-CH), 5.05 (s, 2,2′-CH), 7.91 (s, exo aromatic), 8.65 (s, imine). ^{13}C NMR (50.54 MHz, CD_3CN, δ (ppm)): 35.5 (NCH_2CH_2S), 58.7 (benzylic), 65.1 (NCH_2CH_2S), 71.2−73.9 (2,2′ and 3,3′ aromatic), 78.8 (imine aromatic), 133.5 (exo aromatic), 134.7 (quaternary C), 165.3 (imine).

[Cu$_2$(1,1/1,2-FeEnFe)](ClO$_4$)$_2$·H$_2$O (7). Reaction (in analogy to the synthesis of **6**, see above) of a mixture of **4** (0.5 g, 0.67 mmol) with [Cu(CH_3CN)$_4$]ClO_4 (0.41 g, 1.2 mmol) lead to a red-purple powder. Yield: 0.61 g (0.53 mmol, 85%). Anal. Calcd for $C_{38}H_{44}N_4S_4Fe_2Cu_2Cl_2O_8\cdot H_2O$: C, 40.09; H, 4.28; N, 5.09. Found: C, 40.01; H, 4.06; N, 4.92. IR (KBr): $\tilde{\nu}^{-1}$ [cm^{-1}] 1626 s, 1248 s, 1070−1120 s, 835 s, 610 m. UV (CH_3CN) λ_{max} nm (ϵ, M^{-1} cm^{-1}): 235 (17.9), 257−263 (10.5), 277−285 (8.9), 325−335 (4.4), 364−380 (2.0), 463−469 (1.0). MS (FAB): 1022 (1, M − ClO_4^-), 460 (10, $C_{19}H_{20}S_2N_2CuFe$). ^{1}H NMR (200.13 MHz, CD_3CN, δ (ppm)): 3.19 (m, NCH_2CH_2S), 3.72 (s, methylene bridge), 3.84 (m, NCH_2CH_2S), 4.44 (s, 3,3′-CH), 4.63 (s, 2,2′-CH), 8.65 (s, imine). ^{13}C NMR (50.54 MHz, CD_3CN, δ (ppm)): 34.7 (methylene bridge), 35.5 (NCH_2CH_2S), 58.3 (NCH_2CH_2S), 69.6−71.3 (2,2′ and 3,3′ aromatic), 77.9 (imine aromatic), (quaternary C), 117.5 (1,2:1′,2′-isomer quaternary C, 134.3 (1,1′:2,2′-isomer quaternary C), 169.9 (imine).

[Cu$_2$(FeMeFe)](ClO$_4$)$_2$ (8). Reaction of **(5)** (0.25 g, 0.32 mmol) (in analogy to the synthesis of **6**, see above) reacts with [Cu(CH_3CN)$_4$]ClO_4 (0.21 g, 0.65 mmol) yielded a red-purple, air-sensitive powder. Yield: 0.30 g (0.27 mmol, 85%). IR (KBr): $\tilde{\nu}^{-1}$ [cm^{-1}] 3080 w, 1623 s, 1248 s, 1070−1150 s, 838 s, 620 m. UV (CH_3CN) λ_{max} nm (ϵ, M^{-1} cm^{-1}): 228 (15.2), 257−267 (16.6), 280−300 (5.3), 320−340 (3.4), 362−382 (1.9), 463−471 (1.0). ^{1}H NMR (200.13 MHz, CD_3NO_2, δ (ppm)): 3.07 (s, methylene bridge), 3.31 (m, NCH_2CH_2S), 4.00 (m, NCH_2CH_2S), 4.50 (s, 3,3′-CH), 4.86 (s, 2,2′-CH), 8.82 (s, imine). ^{13}C NMR (50.54 MHz, CD_3NO_2, δ (ppm)): 34.6 (methylene bridge), 39.0 (NCH_2CH_2S), 41.0 (quaternary C), 58.7 (NCH_2CH_2S), 71.4−81.4 (2,2′ and 3,3′ aromatic), 79.9 (imine aromatic), 172.7 (imine).

Crystal Structure Determination. Crystals of *endo*-FeBeFe were obtained over a period of 4 months by diffusion of pentane into a solution of the ligand in dichloromethane/pentane (1:1) at −33 °C. A well-shaped orange plate of *endo*-FeBeFe with approximate dimensions 0.55 × 0.30 × 0.04 mm was mounted on a Siemens Stoe AED 2 diffractometer at −70 °C (Table 1). The structure was solved by direct methods (SHELXS86[13]) and refined by least-squares methods based on F^2 (SHELXL97[14]) with 2730 unique reflections, using anisotropic temperature factors for all non-hydrogen atoms. The hydrogen atoms at C1, C6, and C11 were located in a difference Fourier synthesis and refined isotropically. All other hydrogen atoms were inserted in calculated positions and only common isotropic temperature factors were refined.

Table 2. Selected Bond Distances [Å] and Angles [deg] for *endo*-FeBeFe

Bond Distances			
Fe(1)−C(17)	2.028(6)	Fe(1)−C(16)	2.054(6)
Fe(1)−C(21)	2.029(7)	Fe(1)−C(15)	2.056(6)
Fe(1)−C(19)	2.037(7)	N(1)−C(1)	1.266(7)
Fe(1)−C(20)	2.041(7)	N(2)−C(11)	1.260(7)
Fe(1)−C(13)	2.043(7)	C(1)−C(17)	1.488(8)
Fe(1)−C(18)	2.044(7)	C(4)−C(5)	1.506(7)
Fe(1)−C(14)	2.047(7)	C(7)−C(8)	1.494(6)
Fe(1)−C(12)	2.053(6)	C(11)−C(12)	1.467(8)
Angles			
C(3)−S(1)−C(4)	103.3(2)	C(5)−C(4)−S(1)	114.9(3)
C(9)−S(2)−C(8)	102.4(2)	C(7)−C(8)−S(2)	115.0(3)

Results and Discussion

Syntheses and Structural Properties. The new bismacrocylic Schiff-base ligands *exo*/*endo*-FeBeFe (**3**), 1,1/1,2-FeEnFe (**4**), and FeMeFe (**5**) were obtained by condensation of the corresponding tetrathiatetraamines with 1,1′-bisformylferrocene in toluene (see Chart 1). Analytical and spectroscopic data are in agreement with the proposed structures. The ^{1}H NMR spectrum of the ligand with the benzene spacer group (**3**) reveals that the isomers *exo*/*endo*-FeBeFe occur in a 10:3 ratio. The assignment of the two isomers is based on the high field shift of the aromatic protons which are in the macrocyclic ring (*endo*-isomer: 7.00 ppm) or at the periphery (*exo*-isomer: 7.63 ppm). The preference for *exo*-FeBeFe is probably due to steric effects. The isomer ratio of (**4**), 1,1/1,2-FeEnFe is approximately 2.5: 10, based on the ^{13}C NMR data of the quaternary ethylene carbon (1,1-isomer, 134.2 ppm; 1,2-isomer, 116.3 ppm).

The assignment of the NMR data to the two isomers of (**3**) was confirmed by an X-ray crystal structure analysis of *endo*-FeBeFe. An ORTEP[15] plot of the structure is shown in Figure 1, and relevant parameters are listed in Table 2. The structure is centrosymmetric (centroid of the benzene spacer group). The angle between the benzene spacer group and the average of the four cyclopentadienyl rings is 46°. The two ferrocenyl groups

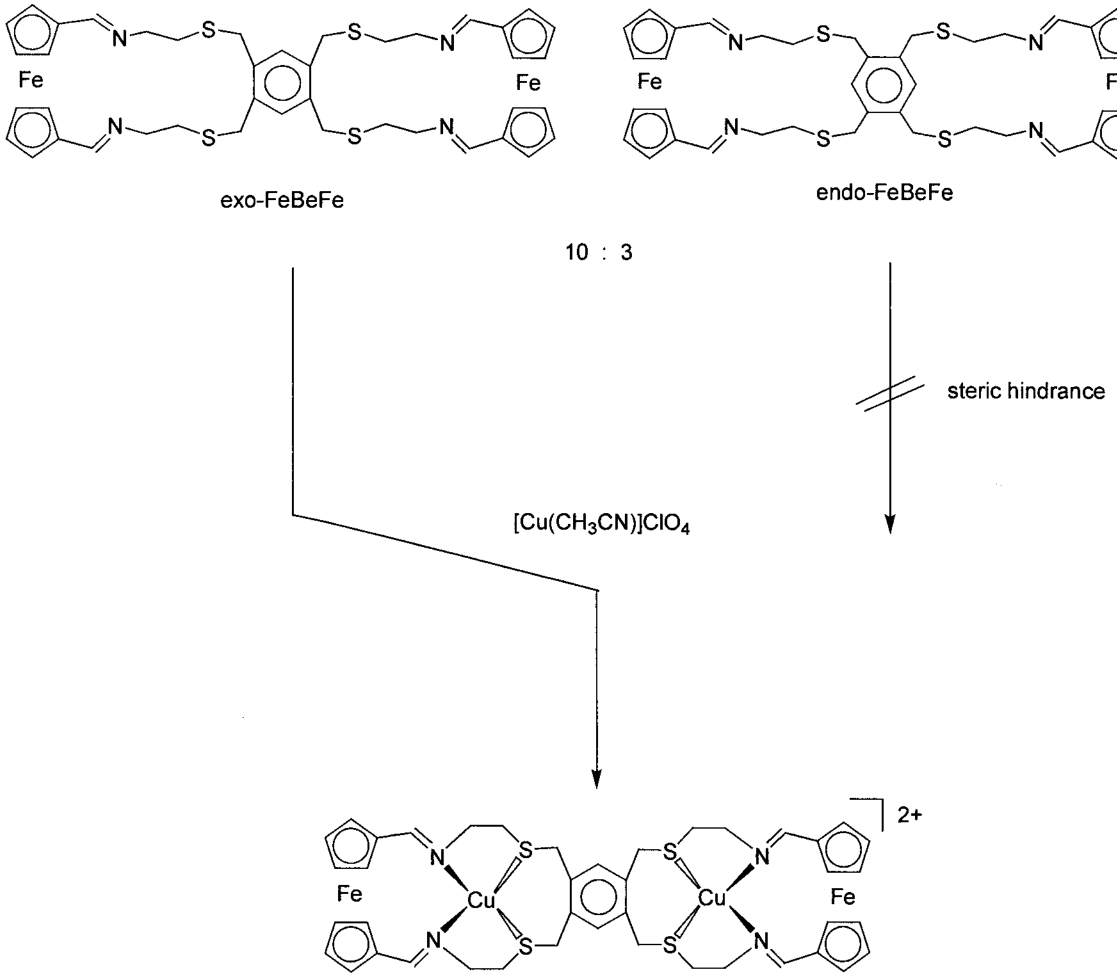
---

(13) Sheldrick, G. M. *SHELIX-86: Program for crystal structure determination*; University Göttingen: Germany, 1986.

(14) Sheldrick, G. M. *SHELIX-97: Program for crystal structure determination*; University Göttingen: Germany, 1997.

(15) Johnson, C.K. *ORTEP: A Thermal Ellipsoid Plotting Program*; Oak Ridge National Laboratory: Oak Ridge, TN, 1965.

Chart 2



are parallel to each other; the cyclopentadienyl rings are tilted by 5° and twisted by 78° (imine substituents). The thioether donors of the macrocyclic rings are, as expected exodentate and the iron···iron distance is 18.03 Å. The iron chromophores are as expected for ferrocene derivatives (see Table 2).

Coordination of copper(I) to the isomer mixture of (**3**) (*exo*/*endo*-FeBeFe) yields a single isomer of the dicopper(I) compound (**6**). As expected, the *endo*-isomer with the two duryl protons directed toward the copper(I) centers is considerably less stable (Chart 2). The ^{1}H NMR spectrum of the isomerically pure *exo*-**6** shows a single signal for the protons of the benzene spacer group (7.91 ppm), the typical high field shift for the proton of the coordinated imine group[6] and the expected signals for the ferrocene groups and the aliphatic part of the ligand backbone.

Cyclic Voltammetry. The electrochemical behavior was investigated at room temperature by cyclic voltammetry at a rotating disk electrode in dichloromethane or acetonitrile, with $[n\text{-}Bu_4N][PF_6]$ as supporting electrolyte. The electrochemical data are summarized in Table 3.

Table 3. Electrochemical Data[a]

compd	E_{pa},[b] [mV]	E_{pc},[c] [mV]	$10^3\Delta E_{pac}$,[d] [mV]
3	880	790	90
4	910	790	120
6	(1000)	(870)	(130)
7	(1040)	(970)	(70)
8	(1060)	(930)	(130)
ferrocene	655 (628)	535 (556)	120 (72)
1,1′-bisformylferrocene	1240	1090	150

[a] In dichloromethane (**3**, **4**) or acetonitrile (**6**−**8**); in parentheses (0.1 mol dm^{-3} $[n\text{-}Bu_4N][PF_6]$); vs SCE; scan rate 0.1 V s^{-1}. [b] Anodic peak potential. [c] Cathodic peak potential. [d] Difference between anodic and cathodic peak potentials.

The bisferrocenyl macrocyclic ligands **3** and **4** have single oxidation waves (E_{pa}) at 880 and 910 mV (vs SCE), respectively. In the range of 50−800 mV s^{-1} the peak positions and the peak separations are approximately independent of the scan rate, and these results may be interpreted as being due to reversible two electron oxidation processes, centered at the ferrocenyl groups, that is, the two iron centers are, as expected, independent. The observed potentials are in the expected range (−100 to +1250 mV vs SCE)[16] (see also Table 3). The dicopper(I) compounds **6**, **7**, and **8** also have a single reversible oxidation wave (see Table 3), that is, in the potential window of acetonitrile (−1900 to +1800 mV) there is only the one relevant oxidation wave listed in Table 3 (in addition, at −500 mV there is the characteristic Cu^0/Cu^I stripping peak). Interestingly, for the dicopper(I) compounds there is an anodic shift of the oxidation waves by over 100 mV (note that, due to solubility problems, the solvent used for the copper-free ligands and the dicopper(I) complexes is different; the expected solvent effect is around 30 mV, see Table 3). Thus, the single oxidation wave (two electron oxidation process) lies between that of the copper-free ferrocenyl ligand (see Table 3) and that expected for a similar dicopper(I) couple without ferrocenyl end groups (approximately

---

(16) Togni, A.; Hayashi, T. *Ferrocenes: Homogeneous catalysis, organic synthesis, materials science*; VCH: New York, 1995.

Table 4. Infrared Data[a]

compd	out-of-plane bending [cm^{-1}]
3	811
4	810
5	808
6	830
7	835
8	838

[a] IR spectra were measured with KBr disks.

1300 mV).[6] For ferrocene/copper(I) couples, similar to those reported here, shifts of the ferrocene oxidation waves toward more positive potentials have generally been observed, but usually two independent waves for the oxidation of copper(I) and ferrocene were reported.[5a,17] There is, however, a recently reported compound with a rather short copper−iron distance (3.23 Å; models indicate that the copper−iron distances in the compounds reported here is around 4 Å) which shows electrochemical behavior that is similar to that reported here, except that there is a stabilization of the reduced form by 500 mV.[18] As a whole, the electrochemical data suggest that there is a copper−iron interaction but the metal−metal coupling is rather small.

IR Spectroscopy. The C−H out-of-plane bending vibration in ferrocene (815 cm^{-1}) is shifted to higher energies (851 cm^{-1}) in the ferricenium ion, Thus, IR spectroscopy is a powerful probe for the assignment of the oxidation state of the iron atom in ferrocene derivates.[19] The corresponding transitions of the Cu(I) compounds **6**, **7**, and **8** were shifted by 20−30 cm^{-1} to higher energy in comparison to those of the corresponding copper-free ligands (see Table 4). This shift to higher energy reflects the occurrence of a perturbation of the iron center through the imine functions, when they are coordinated to the copper centers.

Mössbauer Spectroscopy. The isomer shift and quadrupole splitting values in ^{57}Fe Mössbauer spectra (100 K) of the metal complexes **6**, **7**, and **8** are summarized in Table 5, where the corresponding data of ferrocene appear for comparison. There is a small but significant decrease of the quadrupole splitting parameters of the dicopper(I) compounds in comparison with the value of ferrocene. The relatively small difference suggests that the copper centers coordinated to the azathia macrocycles in close neighborhood to the iron centers are only weakly coupled to the ferrocene units.

Table 5. Mössbauer Spectral Data (at 100 K)

compd	IS [mm s^{-1}]	QS [mm s^{-1}]
6	0.52	2.19
7	0.52	2.25
8	0.53	2.17
ferrocene	0.53	2.37

Conclusion

Three bismacrocyclic ligands with two N_2S_2 donor sets each (imine/thioether), two ferrocenyl end groups, and benzene, ethene, or spirocarbon spacer groups have been synthesized and characterized. From the possible isomers, one of each ligand yields heterotetranuclear compounds with copper(I) salts. Models based on the X-ray structure of one of the ligands indicate that the copper−iron distances are around 4 Å, and electrochemistry, IR spectroscopy, and Mössbauer spectroscopy indicate that there is a small but significant iron−copper interaction in the three tetranuclear compounds studied here (Table 5).

Acknowledgment. Generous financial support by the German Science Foundation (DFG) is gratefully acknowledged.

Supporting Information Available: An X-ray crystallographic file, in CIF format, for the complex (*endo*-FeBeFe) is available free of charge via the Internet at http://pubs.acs.org. given on any current masthead page.

IC981389I

---

(17) Beer, P. D.; Nation, J. N.; Mcwhinnie, S. L. W.; Harman, M. E.; Hursthouse, M. B.; Ogden, M. I.; White; A. H. *J. Chem. Soc., Dalton Trans* **1991**, 2485.

(18) Siemeling, U. *J.Chem. Soc., Dalton Trans* **1997**, 4705.

(19) Akabori, S.; Kumagai, T.; Shirashige, S.; Sato, S.; Kawazoe, C.; Tamura, C.; Sato, M. *Organometallics* **1987**, *6*, 526.