# Effect of Ligand Constraints on the Geometry of Two Sulfur-Bridged Binuclear Iron(II) Complexes. The Structures of Bis{μ-[$N,N'$-dimethyl-$N,N'$-bis(β-mercaptoethyl)ethylenediamine]}-diiron(II) and Bis{μ-[$N,N'$-dimethyl-$N,N'$-bis(β-mercaptoethyl)-1,3-propanediamine]}-diiron(II)

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**Abstract:** The crystal and molecular structures of two high-spin ferrous complexes, bis{μ-[$N,N'$-dimethyl-$N,N'$-bis(β-mercaptoethyl)ethylenediamine]-diiron(II), (FeL)$_2$, and bis{μ-[$N,N'$-dimethyl-$N,N'$-bis(β-mercaptoethyl)-1,3-propanediamine]}-diiron(II), (FeL')$_2$, are reported. (FeL')$_2$ crystallizes as red-brown parallelepipeds in space group $P2_1/c$. The cell parameters are $a = 9.538$ (1) Å, $b = 11.636$ (1) Å, $c = 12.248$ (1) Å, and $\beta = 115.54$ (1)°. The measured density is 1.497 (2) g/cm$^3$ in agreement with the calculated value of 1.496 (1) g/cm$^3$ for four Fe-(C$_9$H$_{20}$N$_2$S$_2$) formulas in the unit cell. The structure has been refined to $R_1 = 0.059$ and $R_2 = 0.085$ based on 1532 independent observed reflections. The molecule is a dimercapto-bridged dimer with an iron–iron distance of 3.371 (2) Å. The coordination geometry about each of the iron atoms is a slightly distorted trigonal bipyramid. (FeL)$_2$ has the same space group with cell constants $a = 9.202$ (4) Å, $b = 11.080$ (7) Å, $c = 12.418$ (6) Å, and $\beta = 112.62$ (2)°. The measured density is 1.495 (5) g/cm$^3$ and the calculated density is 1.490 (3) g/cm$^3$ for four Fe(C$_8$H$_{18}$N$_2$S$_2$) formulas per unit cell. Its structure was solved based on 738 independent reflections and refined to $R$ values of 0.074 and 0.083. With the same N$_2$S$_3$ donor atom set as (FeL')$_2$, the coordination geometry of (FeL)$_2$ is much more distorted from that of a trigonal bipyramid. Elimination of one methylene group between the two nitrogen donor atoms has caused a 15° decrease of the axial–metal–axial angle and deformation of the Fe$_2$S$_2$ rhombus. The iron–iron nonbonded distance is shortened significantly from 3.371 (2) Å in (FeL')$_2$ to 3.206 (5) Å in (FeL)$_2$, accompanied by a decrease in the bridging angle Fe–S1–Fe' from 86.91 (8)° in (FeL')$_2$ to 82.7 (2)° in (FeL)$_2$. These results demonstrate that external ligand constraints can influence the geometry of a binuclear Fe$_2$S$_2$ system.

The variation of metal–metal distance with electronic configuration has previously been established for low-spin sulfur-bridged iron dimers where strong metal–metal bonding can occur.[1–3] Here we report that the metal–metal distance in binuclear Fe$_2$(SR)$_2$ complexes can also be influenced by geometric constraints when the bridging sulfur atom is part of a tetradentate chelating ligand. This work is part of a continuing investigation of iron–sulfur coordination compounds and proteins.[4]

A tetradentate ligand system with an N$_2$S$_2$ donor atom set was employed. Two ligands, $N,N'$-dimethyl-$N,N'$-bis(β-mercaptoethyl)ethylenediamine (LH$_2$) and $N,N'$-dimethyl-$N,N'$-bis(β-mercaptoethyl)-1,3-propanediamine (L'H$_2$), were synthesized.[5] As anticipated from



LH$_2$        L'H$_2$
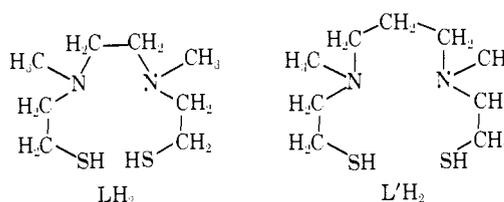
a careful examination of molecular models and subsequently demonstrated by the structural analysis of a zinc derivative,[6] [Zn$_2$LCl$_2$]$_2$·2H$_2$O, complexes of the former ligand are sterically strained. The strain may be judged by anomalously small bond angles imposed by the chelate rings and by other geometric criteria discussed in detail below. In complexes of L', the strain was expected to be relieved by the presence of the additional methylene group in the N,N chelate ring.

The synthesis and chemical and physical properties of the iron derivatives [Fe(C$_8$H$_{18}$N$_2$S$_2$)]$_2$,(Fe L)$_2$, and [Fe(C$_9$H$_{20}$N$_2$S$_2$)]$_2$, (FeL')$_2$, will be the subject of future communications.[7] Here we report the molecular

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(2) D. Coucouvanis, S. J. Lippard, and J. A. Zubieta, *Inorg. Chem.*, **9**, 2775 (1970).

(3) N. G. Connelly and L. F. Dahl, *J. Amer. Chem. Soc.*, **92**, 7472 (1970).

(4) S. J. Lippard, *Accounts Chem. Res.*, **6**, 282 (1973), and references therein.

(5) The ligands were prepared by a modification of the method of D. D. Reynolds, M. K. Massad, D. L. Fields, and D. J. Johnson, *J. Org. Chem.*, **26**, 5109 (1961).

(6) W. J. Hu, D. Barton, and S. J. Lippard, *J. Amer. Chem. Soc.*, **95**, 1170 (1973).

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structures of these two binuclear, sulfur-bridged $Fe_2S_2$ complexes which display quite different metal–metal distances and coordination geometries.

## Experimental Procedure and Results

Bis{ $\mu$-N,N'-dimethyl-N,N'-bis($\beta$-mercaptoethyl)-1,3-propanediamine]}-diiron(II), [Fe(C$_9$H$_{20}$N$_2$S$_2$)]$_2$. Collection and Reduction of Data. The compound crystallized as red-brown parallelepipeds. Crystals of both the oxygen-sensitive compounds (FeL')$_2$ and (FeL)$_2$ decompose in the air much more slowly than in solution or as fine powders. This slower decomposition rate permitted examination on the precession camera to be done in the air. From precession photographs taken using Cu K$\alpha$ radiation, the absences $h0l$, $l \neq 2n$, and $0k0$, $k \neq 2n$, established the space group to be $P2_1/c$ ($C^5_{2h}$). A crystal of approximate dimensions of $0.1 \times 0.12 \times 0.13$ mm was sealed in a glass capillary under a nitrogen atmosphere and used for intensity measurements. Employing Cu K$\alpha_1$ radiation ($\lambda$ 1.5405 Å) 12 reflections were centered on a FACS-I-DOS diffractometer and the setting angles were used in a least-squares refinement of the cell constants. The results are $a = 9.538$ (1) Å, $b = 11.636$ (1) Å, $c = 12.248$ (1) Å, and $\beta = 115.54$ (1)°. The density measured by flotation in mixtures of bromoform and carbon tetrachloride was 1.497 (2) g/cm$^3$, in agreement with the calculated value of 1.496 (1) g/cm$^3$ for four Fe(C$_9$H$_{20}$N$_2$S$_2$) formulas in the unit cell.

The mosaicity of the crystal was measured by means of narrow-source, open counter, $\omega$ scans. For nine arbitrarily chosen low-order, strong reflections, the width at half-height ranged from 0.05 to 0.12° (average 0.07°) which is acceptably low.[8]

The intensities were measured using Ni-filtered Cu K$\alpha$ radiation by the $\theta$–$2\theta$ scan technique at a takeoff angle of 2.3°. At this angle the intensity of radiation was about 85% of the maximum as a function of takeoff angle. A $4.5 \times 4.5$ mm aperture was used and positioned in front of the counter 31 cm from the crystal. A symmetric scan range of 1.25° in $2\theta$ was used plus the angular separation of K$\alpha_1$ and K$\alpha_2$. The scan speed was 1°/min. Stationary counter, stationary crystal background counts of 10 sec were taken at each end of the scan. Aluminum-foil attenuators of varying thickness were inserted automatically when the intensity of the reflection exceeded about 10,000 counts/sec during the scan in order to eliminate saturation of the counter circuit.

Data were measured out to a $2\theta$ value of 125°. The intensities of three standard reflections, (400), (040), and (006), were measured after every 97 reflections. In no case did the intensity of a standard reflection vary by more than $\pm 2.8\%$ of its mean, and no systematic trend was observed. A total of 2233 data points were collected including the equivalent ($hk0$) and ($\bar{h}k0$) reflections.

The observed intensities were corrected for background, use of attenuators, Lorentz, polarization, and absorption effects ($\mu = 128.0$ cm$^{-1}$).[9] The minimum and maximum transmission factors are 0.224 and 0.408, respectively. The agreement factor based on $F^2$ for the 186 ($hk0$) and ($\bar{h}k0$) reflection pairs was improved from 0.108 to 0.058 after the absorption correction. A Wilson plot subsequently yielded an approximate absolute scale factor. The scattering factors used were for neutral atoms;[10] corrections for anomalous dispersion effects for the iron and sulfur atoms were taken from the compilation of Cromer[11] and applied to the calculated structure factor amplitudes.

The integrated intensity corrected for background and attenuators is given by $I$, the standard deviation of which, $\sigma(I)$, was obtained from the expression

$$\sigma(I) = [E + (T_E/2T_B)^2(B_1 + B_2) + (\epsilon I)^2]^{1/2}$$

where $E$ is the total count in the peak plus background observed for time $T_E$, $B_1$ and $B_2$ are the background counts observed for time $T_B$ at each end of the scan, and $\epsilon$ is an "ignorance factor"[12] assumed in this case to be 0.04. Only reflections which satisfied the condition $I > 3\sigma(I)$ were included in the refinement.

Determination and Refinement of the Structure. The atomic coordinates of the crystallographically independent iron atom and two sulfur atoms were determined from a three-dimensional Patterson synthesis.[9] The positional and isotropic thermal parameters of these three atoms were refined by least squares[9] using unit weights. The remaining nonhydrogen atoms were located in the subsequent electron density difference Fourier map, phased on the three heavy atoms. After refining the scale factor, positional parameters, and individual isotropic thermal parameters with unit weights, subsequent cycles using anisotropic thermal parameters and weights $w = 4F_o^2/\sigma^2(F_o^2)$ converged to values of 0.075 and 0.120 for $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2]^{1/2}$, respectively. In these expressions, $F_o$ and $F_c$ are the observed and calculated structure factor amplitudes and $\sigma(F_o^2)$ is $\sigma(I)/(Lp)$.

An electron density difference map was then synthesized and revealed the location of the 20 hydrogen atoms which were added into the refinement. In the final refinement stage a modification of the weighting scheme was introduced to improve the constancy of the function $\Sigma w(|F_o| - |F_c|)^2$ for various classes of reflections.[13] The empirical function used set $w = (0.11F_o + 3.8)^{-1}$ and five strong reflections ($\bar{1}00$), ($\bar{2}00$), ($\bar{4}00$), (302), and ($\bar{1}11$) were rejected because of possible extinction effects.[14]

In the refinement of the hydrogen positional parameters (hydrogen isotropic thermal parameters were set at 5.0 Å$^2$), H21, H32, H61, and HM11[15] were found to oscillate about their equilibrium positions while all other 16 hydrogen atoms refined well. Therefore in the final refinement these four hydrogen atoms were fixed in idealized positions (C–H = 0.95 Å, <H–C–N = 109.5°)[16] while other hydrogen positions and all nonhydrogen parameters were refined. The atomic parameter shifts of the 16 refined hydrogen atoms were on the order of 0.1 of their standard deviations in the last cycle. The final residuals are $R_1 = 0.059$ and $R_2 = 0.085$ with $[\Sigma w(|F_o| - |F_c|)^2/(NO - NV)]^{1/2} = 0.922$ based on 1532 independent reflections. The positional and thermal parameters are listed in Tables I and II and the root-mean-square vibrational amplitudes in Table III (see paragraph regarding supplementary material at the end of this paper).

Bis{ $\mu$-[N,N'-dimethyl-N,N'-bis($\beta$-mercaptoethyl)ethylenediamine]}-diiron(II), [Fe(C$_8$H$_{18}$N$_2$S$_2$)]$_2$. Collection and Reduction of Data. Preliminary examination by precession photography (Cu K$\alpha$ radiation) established that the red-brown crystals are monoclinic with space group $P2_1/c$ ($C^5_{2h}$). The unit cell parameters were then refined by a least-squares technique to give the best fit between calculated and observed settings $\chi$, $\phi$, and $2\theta$ for 10 independent reflections centered on a Picker full-circle automated X-ray diffractometer (four-angle programmer) using Cu K$\alpha$ ($\lambda$ 1.5418 Å) radiation[17] and a crystal sealed in a capillary under a nitrogen atmosphere. The cell constants are $a = 9.202$ (4) Å, $b = 11.080$ (7) Å, $c = 12.418$ (6) Å, and $\beta = 112.62$ (2)°. The measured density was 1.495 (5) g/cm$^3$ (by flotation in bromoform–carbon tetrachloride mixtures) and the calculated density is 1.490 (3) g/cm$^3$ for four Fe(C$_8$H$_{18}$N$_2$S$_2$) formulas per unit cell.

A crystal of approximate dimensions of $0.20 \times 0.15 \times 0.11$ mm was mounted along $b^*$ and sealed in a glass capillary under a nitrogen atmosphere and used for data collection. The intensities were measured using Ni-filtered Cu K$\alpha$ radiation ($\lambda$ 1.5418 Å) by the $\theta$–$2\theta$ scan technique to a $2\theta$ value of 102° at the scan rate of 1°/min. The takeoff angle used was 2.6°, a symmetric scan of 1.5° in $2\theta$ plus the angular separation of K$\alpha_1$ and K$\alpha_2$ was used, and individual 10-sec background counts were recorded at both ends of

(8) T. C. Furnas, "Single Crystal Orienter Instruction Manual," General Electric Co., Milwaukee, Wis., 1957.

(9) Programs for the IBM 360-91 computer used in this work include, in addition to various local data reduction routines, the following: ACAC-4, a revised version of the Prewitt absorption correction program; XDATA, the Brookhaven Wilson plot and scaling program; FORDAP, the Zalkin Fourier program; CULS, a local version of the Busing–Martin–Levy structure factor calculation and least-squares refinement program (ORFLS); ORFFE, the Busing–Martin–Levy molecular geometry and error function program; ORTEP, the Johnson thermal ellipsoid plotting program; MEANPLANE, the Pippy–Ahmed best planes program.

(10) H. P. Hanson, F. Herman, J. D. Lee, and S. Skillman, Acta Crystallogr., 17, 1040 (1964).

(11) D. T. Cromer and D. Lieberman, J. Chem. Phys., 53, 1891 (1970).

(12) (a) G. M. Brown and H. A. Levy, J. Physiol. (Paris), 25, 497 (1964); (b) R. D. Ellison and H. A. Levy, Acta Crystallogr., 19, 260 (1965); (c) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, Inorg. Chem., 6, 197 (1967).

(13) D. W. J. Cruickshank in "Computing Methods of Crystallography," J. S. Rollett, Ed., Pergamon Press, New York, N. Y., 1965.

(14) W. H. Zachariasen, Acta Crystallogr., Sect. A, 24, 425 (1968).

(15) Table II, footnote a.

(16) M. R. Churchill, Inorg. Chem., 12, 1213 (1973).

(17) In addition to those cited in ref 9, local versions of MODE-1, the Brookhaven diffractometer setting and cell constant and orientation refinement, GSET, the Prewitt diffractometer setting program, and ACAC-3, a revised version of the Prewitt absorption correction and data reduction program, were used.

Table I. Final Nonhydrogen Atomic Positional and Thermal Parameters for $[Fe(C_9H_{20}N_2S_2)]_2$[a,b]

| | $x$ | $y$ | $z$ | $\beta_{11}$[c,d] | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| Fe | 0.1206 (1) | 0.0903 (1) | 0.1068 (1) | 7.8 (2) | 4.6 (1) | 5.2 (1) | 0.3 (1) | 1.9 (1) | −0.2 (1) |
| S1 | −0.1295 (2) | −0.0053 (2) | 0.0696 (2) | .9.5 (3) | 6.7 (2) | 6.3 (2) | −0.8 (2) | 3.3 (2) | −0.8 (1) |
| S2 | 0.2579 (3) | 0.0162 (2) | 0.3004 (2) | 11.8 (3) | 8.1 (2) | 6.6 (2) | −1.7 (2) | 2.0 (2) | 1.9 (2) |
| N1 | −0.0204 (8) | 0.2487 (6) | 0.0642 (7) | 9.2 (10) | 5.3 (6) | 8.2 (7) | 1.0 (6) | 2.3 (7) | −1.6 (5) |
| N2 | 0.3455 (8) | 0.1995 (6) | 0.1563 (6) | 9.9 (10) | 5.4 (5) | 6.7 (6) | 0.1 (6) | 3.6 (6) | 0.3 (5) |
| C1 | −0.252 (1) | 0.120 (1) | 0.006 (1) | 7.2 (13) | 8.8 (9) | 12.5 (12) | 0.9 (9) | 2.4 (10) | −4.0 (9) |
| C2 | −0.171 (1) | 0.229 (1) | 0.067 (1) | 9.6 (15) | 8.3 (10) | 19.7 (17) | 1.5 (10) | 5.0 (13) | −2.0 (10) |
| C3 | 0.052 (1) | 0.351 (1) | 0.142 (1) | 16.7 (19) | 7.7 (9) | 13.8 (13) | 2.8 (11) | 3.9 (13) | −3.0 (9) |
| C4 | 0.209 (1) | 0.388 (1) | 0.153 (1) | 12.1 (15) | 4.8 (7) | 11.3 (11) | −1.0 (8) | 2.3 (10) | −0.6 7) |
| C5 | 0.339 (1) | 0.305 (1) | 0.224 (1) | 10.9 (13) | 6.5 (8) | 8.6 (9) | −0.7 (8) | 1.7 (9) | −1.3 (7) |
| C6 | 0.471 (1) | 0.125 (1) | 0.237 (1) | 8.4 (13) | 6.6 (7) | 10.1 (10) | 0.4 (8) | 2.6 (9) | 0.6 (7) |
| C7 | 0.448 (1) | 0.079 (1) | 0.345 (1) | 11.5 (14) | 6.9 (8) | 7.0 (8) | −0.4 (9) | 2.4 (9) | −0.1 (7) |
| Me1 | −0.054 (2) | 0.282 (1) | −0.063 (1) | 21.8 (23) | 10.0 (11) | 10.6 (12) | 3 7 (14) | 4.1 (13) | 2.3 (9) |
| Me2 | 0.386 (1) | 0.234 (1) | 0.058 (1) | 13.3 (16) | 8.9 (10) | 9.4 (10) | −0.6 (10) | 5.5 (10) | 1.3 (8 |

[a] Atoms are labeled as indicated in Figure 1. [b] Standard deviations, in parentheses, occur in the last significant figure for each parameter. [c] The form of the anisotropic ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [d] Values reported are $\times 10^3$.

Table II. Final Hydrogen Positional Parameters for $[Fe(C_9H_{20}N_2S_2)]_2$[a,b]

| | $x$ | $y$ | $z$ |
|---|---|---|---|
| H11 | −0.30 (2) | 0.13 (1) | −0.06 (1) |
| H12 | −0.35 (2) | 0.11 (1) | 0.01 (1) |
| H21 | −0.16 | 0.22 | 0.15 |
| H22 | −0.26 (2) | 0.30 (1) | 0.02 (1) |
| H31 | −0.03 (2) | 0.43 (1) | 0.11 (1) |
| H32 | 0.07 | 0.34 | 0.23 |
| H41 | 0.25 (2) | 0.46 (1) | 0.20 (1) |
| H42 | 0.20 (2) | 0.40 (1) | 0.07 (1) |
| H51 | 0.33 (2) | 0.27 (1) | 0.30 (1) |
| H52 | 0.44 (2) | 0.34 (1) | 0.26 (1) |
| H61 | 0.49 | 0.06 | 0.20 |
| H62 | 0.60 (2) | 0.17 (1) | 0.27 (1) |
| H71 | 0.54 (2) | 0.03 (1) | 0.38 (1) |
| H72 | 0.46 (2) | 0.14 (1) | 0.40 (1) |
| HM11 | 0.04 | 0.31 | −0.07 |
| HM12 | −0.14 (2) | 0.20 (1) | −0.10 (1) |
| HM13 | −0.15 (2) | 0.35 (1) | −0.09 (1) |
| HM21 | 0.41 (2) | 0.15 (1) | 0.03 (1) |
| HM22 | 0.29 (2) | 0.29 (1) | 0.01 (1) |
| HM23 | 0.50 (2) | 0.27 (1) | 0.09 (1) |

[a] In this table, H21, for example, refers to the first hydrogen atom attached to C2; HM13 refers to the third hydrogen atom attached to Me1. [b] See footnote b, Table I.

Table III. Root-Mean-Square Amplitudes of Vibration (in Å) for $[Fe(C_9H_{20}N_2S_2)]_2$[a,b]

| Atom | Min | Int | Max |
|---|---|---|---|
| Fe | 0.166 (2) | 0.175 (2) | 0.199 (2) |
| S1 | 0.184 (3) | 0.194 (3) | 0.221 (3) |
| S2 | 0.183 (3) | 0.199 (4) | 0.277 (3) |
| N1 | 0.168 (11) | 0.186 (10) | 0.257 (10) |
| N2 | 0.191 (10) | 0.192 (10) | 0.205 (10) |
| C1 | 0.16 (2) | 0.20 (1) | 0.33 (2) |
| C2 | 0.18 (2) | 0.24 (1) | 0.37 (2) |
| C3 | 0.19 (2) | 0.25 (1) | 0.34 (2) |
| C4 | 0.18 (1) | 0.21 (1) | 0.30 (1) |
| C5 | 0.18 (1) | 0.22 (1) | 0.27 (1) |
| C6 | 0.18 (1) | 0.21 (1) | 0.27 (1) |
| C7 | 0.20 (1) | 0.22 (1) | 0.24 (1) |
| Me1 | 0.22 (2) | 0.29 (2) | 0.32 (2) |
| Me2 | 0.20 (1) | 0.23 (1) | 0.26 (1) |

[a] Taken along the principal axes of the thermal ellipsoids; the orientation of these axes may be seen from Figure 1. [b] See footnotes a and b in Table I.

the scan. A few low order reflections showed structure, indicating some imperfection of the crystal. Several crystals had been examined and they all showed some extent of imperfection so the best one was chosen for data collection. The intensities of four

strong and sharp reflections (242), (32$\bar{1}$), (411), and (10$\bar{6}$) were measured after every 100 reflections to monitor the crystal and instrument stabilities. There was no systematic decline of these intensities. The last three standards varied randomly within $\pm 4\%$ of their mean values and had a combined $\sigma$ (mean) of 3%. The first showed up to 7.6% maximum deviation with a $\sigma$ (mean) of 3.6%. These variations, while approximately equal to the calculated $\sigma(I)$'s for the standards, were somewhat larger than usual, and were probably due either to electronic instability or slight crystal movements. In view of the poor quality of the crystals (vide supra), however, data collection was not interrupted. A total of 1366 reflections was collected, and almost no intensity was observed beyond $2\theta = 102°$.

The observed intensities were corrected for background, use of attenuators, Lorentz, polarization, and absorption effects ($\mu = 134.0$ cm$^{-1}$).[17] The minimum and maximum calculated transmission factors are 0.221 and 0.475, respectively. The agreement factor of the equivalent forms $(0kl)$ and $(0k\bar{l})$ based on $F_o^2$ was improved from 0.210 to 0.100 for 195 reflections after the absorption correction. A Wilson plot subsequently yielded an approximate absolute scale factor.[17] Scattering factors for the zerovalent atoms were obtained from the International Tables.[18] The calculated structure factors were corrected for the effects of anomalous dispersion of the iron and sulfur atoms.[18] The calculation of $\sigma(I)$ is the same as for (FeL')$_2$. Reflections which satisfied the condition $I > 3\sigma(I)$ were included in the refinement, a total of 738 reflections after averaging. The small number of observable reflections is due to the poor scattering character of the crystal and results in fairly large standard deviations in the refinement.

Determination and Refinement of the Structure. The atomic coordinates of the crystallographically independent iron atom and two sulfur atoms were determined for a Patterson synthesis.[17] The positional and isotropic thermal parameters for these three atoms were refined by least squares, with minimization of the function $\Sigma w(|F_o| - |F_c|)^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes and the weights $w$ were taken as $4F_o^2/\sigma^2(F_o^2)$.

A subsequent difference Fourier map yielded the positions of the remaining nonhydrogen atoms. Refinement varying the positional and isotropic thermal parameters led to $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ of 0.113 and a weighted $R$ factor $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2]^{1/2}$ of 0.128. A few cycles using anisotropic thermal parameters converged to $R_1 = 0.093$ and $R_2 = 0.111$. After performing the absorption correction and averaging equivalent reflections, the refinement of all nonhydrogen parameters led to $R_1 = 0.080$ and $R_2 = 0.099$. The resulting structure factors were used to compute a difference Fourier map. The 12 methylene hydrogen atoms were located on the Fourier map and were idealized (C–H = 0.95 Å, $<$N–C–H or $<$C–C–H = 109.5°);[16] their contributions to $F_c$ were included as fixed contributions in subsequent cycles of refinement. After five cycles of refinement, a difference Fourier map was computed, and the six methyl hydrogen atoms were carefully located and kept fixed in the final refinement. In the final six cycles of refinement, all hydrogen position parameters were fixed with their isotropic thermal parameters set at 6.0 Å$^2$ and all the nonhydrogen

(18) "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962, pp 202, 204.

Table IV. Final Nonhydrogen Atomic Positional and Thermal Parameters for $[Fe(C_8H_{18}N_2S_2)]_2{}^{a,b}$

| | $x$ | $y$ | $z$ | $\beta_{11}{}^c$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| Fe | 0.1072 (3) | 0.0903 (3) | 0.0997 (2) | 9.4 (4) | 6.4 (3) | 5.4 (2) | 0.3 (3) | 2.9 (3) | −0.4 (3) |
| S1 | −0.1344 (5) | −0.0242 (4) | 0.0739 (4) | 11.9 (8) | 8.3 (5) | 6.6 (4) | −1.0 (6) | 3.9 (5) | −0.4 (4) |
| S2 | 0.2620 (5) | 0.0117 (5) | 0.2791 (4) | 15.2 (9) | 10.9 (6) | 8.2 (5) | −1.4 (7) | 0.0 (5) | 1.9 (5) |
| N1 | −0.053 (2) | 0.246 (1) | 0.053 (1) | 11 (3) | 8 (2) | 10 (2) | −1 (2) | 3 (2) | 0 (2) |
| N2 | 0.286 (2) | 0.248 (2) | 0.157 (1) | 14 (3) | 12 (2) | 6 (2) | −5 (2) | 3 (2) | −3 (2) |
| C1 | −0.275 (2) | 0.098 (2) | 0.022 (2) | 9 (3) | 15 (3) | 12 (2) | 0 (3) | 5 (2) | −1 (2) |
| C2 | −0.193 (2) | 0.217 (2) | 0.080 (2) | 13 (4) | 9 (2) | 17 (3) | 3 (2) | 7 (3) | −1 (2) |
| C3 | 0.033 (2) | 0.347 (2) | 0.126 (2) | 13 (4) | 6 (2) | 14 (3) | 2 (2) | −3 (3) | −2 (2) |
| C4 | 0.192 (3) | 0.363 (2) | 0.124 (2) | 17 (4) | 8 (2) | 11 (2) | 0 (3) | 1 (3) | 2 (2) |
| C5 | 0.367 (2) | 0.246 (2) | 0.284 (2) | 9 (3) | 11 (3) | 12 (3) | −2 (2) | 2 (2) | −5 (2) |
| C6 | 0.423 (2) | 0.116 (2) | 0.326 (2) | 11 (3) | 15 (3) | 11 (2) | 2 (3) | −1 (2) | −3 (2) |
| Me1 | −0.102 (3) | 0.276 (2) | −0.068 (2) | 31 (5) | 12 (3) | 5 (2) | 4 (3) | 2 (3) | 1 (2) |
| Me2 | 0.405 (2) | 0.244 (2) | 0.102 (2) | 28 (5) | 26 (4) | 14 (3) | −20 (4) | 18 (3) | −14 (3) |

$^a$ Atoms are labeled as indicated in Figure 2. $^b$ Standard deviations, in parentheses, occur in last significant figure for each parameter. $^c$ See footnotes $c$ and $d$, Table I.

Table V. Final Hydrogen Atomic Positional Parameters for $[Fe(C_8H_{18}N_2S_2)]_2{}^{a,b}$

| | $x$ | $y$ | $z$ |
|---|---|---|---|
| H11 | −0.37 | 0.09 | 0.04 |
| H12 | −0.31 | 0.11 | −0.06 |
| H21 | −0.26 | 0.29 | 0.06 |
| H22 | −0.16 | 0.21 | 0.17 |
| H31 | 0.04 | 0.33 | 0.21 |
| H32 | −0.03 | 0.42 | 0.10 |
| H41 | 0.18 | 0.38 | 0.05 |
| H42 | 0.25 | 0.43 | 0.17 |
| H51 | 0.30 | 0.27 | 0.32 |
| H52 | 0.45 | 0.30 | 0.31 |
| H61 | 0.50 | 0.10 | 0.30 |
| H62 | 0.48 | 0.12 | 0.41 |
| HM11 | −0.13 | 0.20 | −0.14 |
| HM12 | −0.19 | 0.32 | −0.14 |
| HM13 | −0.04 | 0.31 | −0.13 |
| HM21 | 0.52 | 0.29 | 0.16 |
| HM22 | 0.39 | 0.16 | 0.04 |
| HM23 | 0.37 | 0.30 | 0.01 |

$^a$ In this table, H21, for example, refers to the first hydrogen atom attached to C2; HM13 refers to the third hydrogen atom attached to Me1. $^b$ See footnotes $a$ and $b$, Table IV.

Table VI. Root-Mean-Square Amplitudes of Vibration (in Å) for $[Fe(C_8H_{18}N_2S_2)]_2{}^{a,b}$

| Atom | Min | Int | Max |
|---|---|---|---|
| Fe | 0.179 (5) | 0.189 (6) | 0.204 (5) |
| S1 | 0.198 (7) | 0.209 (7) | 0.232 (8) |
| S2 | 0.198 (8) | 0.244 (8) | 0.314 (7) |
| N1 | 0.20 (3) | 0.22 (3) | 0.27 (2) |
| N2 | 0.16 (3) | 0.23 (3) | 0.30 (3) |
| C1 | 0.18 (3) | 0.28 (3) | 0.31 (3) |
| C2 | 0.18 (3) | 0.25 (3) | 0.34 (3) |
| C3 | 0.18 (3) | 0.19 (3) | 0.39 (4) |
| C4 | 0.21 (4) | 0.24 (3) | 0.32 (3) |
| C5 | 0.17 (4) | 0.22 (3) | 0.34 (3) |
| C6 | 0.18 (3) | 0.27 (3) | 0.36 (3) |
| Me1 | 0.17 (4) | 0.27 (3) | 0.37 (3) |
| Me2 | 0.10 (5) | 0.19 (4) | 0.51 (3) |

$^a$ Taken along the principal axes of the thermal ellipsoids; the orientation of these axes may be seen from Figure 2. $^b$ See footnotes $a$ and $b$, Table IV.

atomic parameters were refined to give $R$ factors of 0.074 and 0.083. Although the value for $[\Sigma w(|F_o| - |F_c|)^2/(NO - NV)]^{1/2}$ was 2.38, a weighting scheme analysis[13] showed the relative weights to have been satisfactorily assigned. The atomic parameters are listed in Table IV and Table V and the rms thermal amplitudes in Table VI (see footnote regarding supplementary material at the end of this paper).
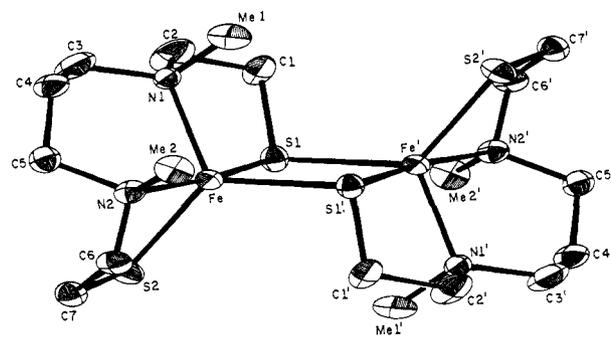


Figure 1. Molecular structure of bis{$\mu$-[$N,N'$-bis($\beta$-mercaptoethyl)-1,3-propanediamine]}-diiron(II) showing the atomic labeling scheme and the 30% probability thermal ellipsoids. Primed and unprimed atoms are related by a crystallographically required inversion center.

## Discussion

**Description of the Structures.** **$[Fe(C_9H_{20}N_2S_2)]_2$.** The molecule $[Fe(C_9H_{20}N_2S_2)]_2$ is a dimercapto-bridged iron dimer as shown in Figure 1. The primed and un-primed atoms are related by a center of symmetry. The bridging atoms Fe, S1, Fe′, S1′ are constrained to be planar by symmetry and the bridging angle Fe–S1–Fe′ is 86.91°. The iron–iron distance of 3.371 (2) Å is comparable to the value of 3.410 (3) Å found for $[Fe(edt)_2]_2{}^{2-}$ which is considered to be too long for metal–metal bonding.[19]

The coordination geometry (Tables VII and VIII) about the iron atoms is best described as a slightly distorted trigonal bipyramid. The atoms N1, S2, and S1′ form the equatorial plane with the iron atom being displaced only 0.037 Å from that plane. The bond angles L–M–L′ in the equatorial plane are 3–8° from 120° (Table VII). The two axial atoms S1 and N2 form a bond angle S1–Fe–N2 of 172.0 (2)°, 8° from the 180° angle expected for ideal trigonal bipyramidal symmetry. The axial–metal–equatorial bond angles range from 83.5 to 95.4°. The angle S1–Fe–N1 (83.8°) is smaller than S1–Fe–S2 (95.4°) and S1–Fe–S1′ (93.1°), indicating that the Fe–S1 bond is tilted with respect to the equatorial plane in the direction of the N1 atom. The variation in the angles S1′–Fe–N2 (94.1°) > N1–Fe–N2 (90.3°) > S2–Fe–N2 (83.5°) shows that the Fe–N2 bond is tilted in the direction of the S2···N1 edge of the equatorial plane. This dis-

(19) M. R. Snow and J. A. Ibers, *Inorg. Chem.*, **12**, 249 (1973); edt$^{2-}$ = ethane-1,2-dithiolate.

**Table VII.** Coordination Geometry of the (FeL')₂ and (FeL)₂ Bond Angles Compared to Regular Trigonal Bipyramid (TBP) (in deg)

| | Regular TBP | [Fe(C₉H₂₀N₂S₂)]₂ᵃ | [Fe(C₈H₁₈N₂S₂)]₂ᵇ |
|---|---|---|---|
| S1–Fe–N2 | 180.0 | 172.0 (2) | 157.6 (4) |
| S1'–Fe–S2 | 120.0 | 122.7 (1) | 121.2 (2) |
| S1'–Fe–N1 | 120.0 | 112.6 (2) | 107.3 (5) |
| S2–Fe–N1 | 120.0 | 124.7 (2) | 130.9 (5) |
| S1–Fe–S2 | 90.0 | 95.41 (8) | 97.0 (2) |
| S1–Fe–N1 | 90.0 | 83.8 (2) | 83.7 (4) |
| S1–Fe–S1' | 90.0 | 93.09 (8) | 97.3 (2) |
| N2–Fe–S2 | 90.0 | 83.5 (2) | 83.6 (4) |
| N2–Fe–S1' | 90.0 | 94.1 (2) | 101.5 (4) |
| N1–Fe–N2 | 90.0 | 90.3 (3) | 79.2 (5) |

ᵃ See footnotes a and b, Table I. ᵇ See footnotes a and b, Table IV.

**Table VIII.** Coordination Geometry of the (FeL')₂ and (FeL)₂ Bond Length Parameters (in Å)

| | [Fe(C₉H₂₀N₂S₂)]₂ᵃ | [Fe(C₈H₁₈N₂S₂)]₂ᵇ |
|---|---|---|
| Fe–S1 | 2.490 (3) | 2.471 (5) |
| Fe–S1' | 2.411 (2) | 2.379 (5) |
| Fe–S2 | 2.325 (2) | 2.304 (5) |
| Fe–N1 | 2.207 (7) | 2.20 (1) |
| Fe–N2 | 2.337 (7) | 2.32 (1) |
| Fe···Fe' | 3.371 (2) | 3.206 (5) |

ᵃ See footnotes a and b, Table I. ᵇ See footnotes a and b, Table IV.

tribution of bond angles is clearly the result of the chelating nature of the ligand since the three smallest bond angles (S1–Fe–N1, S2–Fe–N2, and N1–Fe–N2) are the bite angles of the three chelating rings.

The pattern of metal–ligand bond lengths in this complex can be summarized as follows.

(i) The axial bonds are longer than the equatorial bonds, i.e., Fe–S1 (2.490 Å) > Fe–S1' (2.411 Å), Fe–S2 (2.325 Å), and Fe–N2 (2.337 Å) > Fe–N1 (2.207 Å). The differences are on the order of 20–80 times their standard deviations (Table VIII). This result parallels that for the high-spin, trigonal bipyramidal iron(II) complex [Fe(Me₆tren)Br]⁺, although a good explanation appears to be lacking.[20] One reason for the long Fe–N2 bond in the present case might be to minimize nonbonded contacts between its methyl group and the equatorial atoms, especially S1' (the S1'··· Me2 contact distance is already a short 3.49 (1) Å, Figure 1). In the iron(III) complex [Fe(edt)₂]₂²⁻, the reverse ordering of equatorial > axial bond lengths occurs,[19] again in agreement with structural data on the related d⁵ high-spin, trigonal bipyramidal complex [Mn(Me₆tren)Br]⁺.[20] The longer mean Fe–S bond length in (FeL')₂, 2.41 Å, compared to the average value of 2.29 Å in [Fe(edt)₂]₂²⁻, is consistent with the longer covalent radius expected for high-spin iron(II) vs. high-spin iron(III).

(ii) The bridging bonds Fe–S1 (2.490 Å) and Fe–S1' (2.411 Å) are longer than the nonbridging bond, Fe–S2 (2.325 Å). This result parallels that found for [Fe(edt)₂]₂²⁻,[19] where the average bridging Fe–S distance is 2.39 Å and the nonbridging Fe–S bond length is 2.24 Å. The Fe–S bond lengths in bis(imidotetramethyldithiodiphosphino-S,S)iron(II), the only other

(20) P. L. Orioli, *Coord. Chem. Rev.*, **6**, 285 (1971).

**Table IX.** Ligand Geometry of (FeL')₂ and (FeL)₂

| (FeL')₂ᵃ | | (FeL)₂ᵇ | |
|---|---|---|---|
| **Nonbonded Distances, Å** | | | |
| S1···S1' | 3.558 (4) | S1···S1' | 3.641 (9) |
| S1···S2 | 3.563 (3) | S1···S2 | 3.579 (6) |
| S1···N1 | 3.144 (7) | S1···N1 | 3.12 (2) |
| S1···N2 | 4.815 (7) | S1···N2 | 4.70 (2) |
| S1'···S2 | 4.156 (3) | S1'···S2 | 4.081 (7) |
| S1'···N1 | 3.844 (7) | S1'···N1 | 3.69 (2) |
| S1'···N2 | 3.477 (7) | S1'···N2 | 3.64 (2) |
| S2···N1 | 4.014 (7) | S2···N1 | 4.10 (2) |
| S2···N2 | 3.104 (7) | S2···N2 | 3.08 (2) |
| N1···N2 | 3.223 (9) | N1···N2 | 2.88 (2) |
| **Bond Lengths, Å** | | | |
| S1–C1 | 1.83 (1) } av 1.81 | S1–C1 | 1.81 (2) } av 1.80 |
| S2–C7 | 1.80 (1) | S2–C6 | 1.79 (2) |
| N1–C2 | 1.47 (1) | N1–C2 | 1.49 (2) |
| N1–C3 | 1.49 (1) | N1–C3 | 1.46 (2) |
| N1–Me1 | 1.50 (1) } av 1.48 | N1–Me1 | 1.44 (2) } av 1.48 |
| N2–C5 | 1.50 (1) | N2–C4 | 1.50 (2) |
| N2–C6 | 1.46 (1) | N2–C5 | 1.47 (2) |
| N2–Me2 | 1.47 (1) | N2–Me2 | 1.49 (2) |
| C1–C2 | 1.50 (2) | C1–C2 | 1.55 (3) |
| C3–C4 | 1.51 (2) } av 1.51 | C3–C4 | 1.49 (3) } av 1.53 |
| C4–C5 | 1.51 (1) | C5–C6 | 1.56 (3) |
| C6–C7 | 1.53 (1) | | |
| **Bond Angles, deg** | | | |
| Fe–S1–C1 | 96.2 (4) | Fe–S1–C1 | 98.3 (6) |
| Fe'–S1–C1 | 102.2 (4) | Fe'–S1–C2 | 102.5 (7) |
| Fe–S2–C7 | 102.0 (3) | Fe–S2–C6 | 101.5 (7) |
| Fe–N1–C2 | 111.6 (6) | Fe–N1–C2 | 109 (1) |
| Fe–N1–C3 | 116.6 (6) | Fe–N1–C3 | 107 (1) |
| Fe–N1–Me1 | 107.1 (6) | Fe–N1–Me1 | 111 (1) |
| C2–N1–C3 | 107.1 (8) | C2–N1–C3 | 110 (2) |
| C2–N1–Me1 | 106.8 (9) | C2–N1–Me1 | 110 (2) |
| C3–N1–Me2 | 107.2 (9) | C3–N1–Me1 | 110 (2) |
| Fe–N2–C5 | 109.6 (5) | Fe–N2–C4 | 107 (1) |
| Fe–N2–C6 | 104.4 (5) | Fe–N2–C5 | 109 (1) |
| Fe–N2–Me2 | 118.0 (6) | Fe–N2–Me2 | 113 (1) |
| C5–N2–C6 | 109.2 (8) | C4–N2–C5 | 108 (2) |
| C5–N2–Me2 | 108.4 (8) | C4–N2–Me2 | 110 (2) |
| C6–N2–Me2 | 106.9 (7) | C5–N2–Me2 | 109 (2) |
| S1–C1–C2 | 111.4 (7) | S1–C1–C2 | 109 (1) |
| N1–C2–C1 | 115.0 (9) | N1–C2–C1 | 112 (2) |
| N1–C3–C4 | 116.6 (9) | N1–C3–C4 | 113 (2) |
| C3–C4–C5 | 114.0 (9) | N2–C4–C3 | 111 (2) |
| N2–C5–C4 | 115.2 (8) | N2–C5–C6 | 110 (2) |
| N2–C6–C7 | 114.3 (8) | S2–C6–C5 | 111 (1) |
| S2–C7–C6 | 112.7 (6) | | |
| **Magnitude of Torsion Angles, deg** | | | |
| Fe–S1–C1–C2 | 35 (11) | Fe–S1–C1–C2 | 33 (1) |
| S1–C1–C2–N1 | 56 (1) | S1–C1–C2–N1 | 60 (2) |
| C1–C2–N1–Fe | 44 (1) | C1–C2–N1–Fe | 54 (2) |
| C2–N1–Fe–S1 | 14.5 (7) | C2–N1–Fe–S1 | 24 (1) |
| N1–Fe–S1–C1 | 10.5 (4) | N1–Fe–S1–C1 | 5.1 (7) |
| Fe–N1–C3–C4 | 55 (1) | Fe–N1–C3–C4 | 49 (2) |
| N1–C3–C4–C5 | 70 (1) | N1–C3–C4–N2 | 54 (2) |
| C3–C4–C5–N2 | 78 (1) | | |
| C4–C5–N2–Fe | 64 (1) | C3–C4–N2–Fe | 29 (2) |
| C5–N2–Fe–N1 | 39.8 (6) | C4–N2–Fe–N1 | 3 (1) |
| N2–Fe–N1–C3 | 36.6 (8) | N2–Fe–N1–C3 | 24 (1) |
| Fe–S2–C7–C6 | 16.8 (7) | Fe–S2–C6–C5 | 35 (2) |
| S2–C7–C6–N2 | 49 (1) | S2–C6–C5–N2 | 57 (2) |
| C7–C6–N2–Fe | 52.9 (8) | C6–C5–N2–Fe | 47 (2) |
| C6–N2–Fe–S2 | 31.7 (5) | C5–N2–Fe–S2 | 21 (1) |
| N2–Fe–S2–C7 | 7.5 (4) | N2–Fe–S2–C6 | 7.6 (8) |

ᵃ See footnotes a and b, Table I. ᵇ See footnotes a and b, Table IV.

structurally characterized high-spin iron(II) sulfur complex, range from 2.339 (3) to 2.380 (3) Å.[21]

The ligand geometry of (FeL')₂ is summarized in Table IX. Atoms C1 and C2 are on the opposite sides of the N1–Fe–S1 plane with distances +0.33 (1) and

(21) M. R. Churchill and J. Wormald, *Inorg. Chem.*, **10**, 1778 (1971).

−0.35 (1) Å, respectively, from the plane, indicating that the C2–N1–Fe–S1–C1 five-membered ring has a symmetric skew conformation.[22] Atoms C6 and C7 are on the same side of the N2–Fe–S2 plane with distances of +0.75 (1) and +0.23 (1) Å, respectively, indicating an asymmetric envelope conformation for the C6–N2–Fe–S2–C7 chelate ring. In the six-membered diamine chelate ring, the iron atom and the middle methylene carbon atom C4 are on opposite sides of the best plane calculated for the N1, N2, C3, and C5 atoms, with distances of −0.936 (1) and +0.73 (1) Å, respectively, from the plane. This result shows a symmetric chair conformation for the diamine ring. The two methyl groups are both axial and on the same side of the N1–N2–C3–C5 plane, with distances of +1.39 (1) and +1.41 (1) Å from the plane.

[Fe(C$_8$H$_{18}$N$_2$S$_2$)]$_2$. The structure of [Fe(C$_8$H$_{18}$N$_2$S$_2$)]$_2$ is also a centrosymmetric pentacoordinated dimeric system with the Fe$_2$S$_2$ bridging unit. The labeling of this molecule (Figure 2) is similar to that for (FeL′)$_2$, except that there are now only two methylene groups (C3, C4) between the two donor nitrogen atoms. All bonded iron–sulfur and iron–nitrogen distances are comparable with those of (FeL′)$_2$ and exhibit the same bond length pattern (Table VIII). When comparing the bond angles, however, it is apparent that (FeL)$_2$ is much more distorted from regular trigonal bipyramidal geometry (Table VII). The large changes of the S1–Fe–N2 angle from 172.0 (2)° in (FeL′)$_2$ to 157.6 (4)° in (FeL)$_2$ and of the N1–Fe–N2 angle from 90.3 (3)° in (FeL′)$_2$ to 79.2 (5)° in (FeL)$_2$ show that eliminating one methylene group between the donor atoms N1 and N2 has forced the axial (S1)–equatorial (N1)–axial (N2) ligand chain to wrap more tightly around the iron atom.

The ligand geometry of (FeL)$_2$ is summarized in Table IX. Atoms C1 and C2 are on opposite sides of the N1–Fe–S1 plane with distances of +0.16 (2) and −0.56 (2) Å from the plane. Atoms C5 and C6 are also on opposite sides of the N2–Fe–S2 plane with distances of −0.48 (2) and +0.23 (2) Å from the plane.

The two C–N–Fe–S–C rings, therefore, have asymmetric skew conformations.[22] In the five-membered diamine ring, C4 is only +0.07 Å from the N1–Fe–N2 plane and C3 is displaced by −0.56 Å to the other side. The small torsion angle C4–N2–Fe–N1 of 2.9° reflects the fact that this chelate ring has an asymmetric envelope conformation with C3 as the flap tip.[22] The two methyl groups are on the same side of the N1–Fe–N2 plane as in (FeL′)$_2$, a result which differs from the zinc structure, [Zn$_2$Cl$_2$L]$_2$·2H$_2$O,[6] where the two methyl groups are on opposite sides of the diamine chelate ring.

**Comparison of the Structures and Discussion of Steric Strain.** Hawkins[23] and Busch[24] have performed conformational studies on metal complexes containing various bidentate diamine chelate rings. This kind of calculation has not yet been carried out on complexes containing multidentate ligands. However, the diamine ring conformations, and especially the N–M–N angles,

(22) C. J. Hawkins, "Absolute Configuration of Metal Complexes," Wiley-Interscience, New York, N. Y., 1971.
(23) (a) J. R. Gollogly and C. J. Hawkins, *Inorg. Chem.*, 8, 1168 (1969); (b) *ibid.*, 9, 576 (1970); (c) *ibid.*, 10, 317 (1971); (d) *ibid.*, 11, 156 (1972).
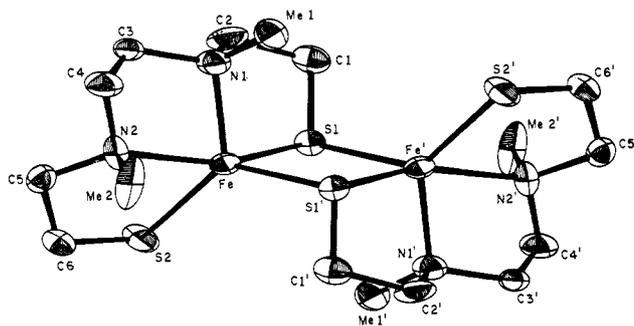(24) L. J. DeHayes and D. H. Busch, *Inorg. Chem.*, 12, 1505 (1973).

**Figure 2.** Molecular structure of bis{μ-[N,N′-dimethyl-N,N′-bis(β-mercaptoethyl)ethylenediamine]}-diiron(II). See caption to Figure 1.

in the three structures [Zn$_2$Cl$_2$L]$_2$·2H$_2$O, (FeL)$_2$, and (FeL′)$_2$ are in excellent agreement with the calculated minimum energy conformations of five (or six)-membered diamine chelate rings.[23,24] The six-membered diamine ring of the (FeL′)$_2$ complex has a chair conformation. For chelate rings formed by 1,3-propane-diamine in its octahedral mono, bis, and tris complexes, the chair conformation is found to be more stable than the boat or skew boat conformation both by minimum energy calculations and experimentally by X-ray studies.[23d] For the five-membered diamine rings, an increase in the average M–N distance from 2.09 Å in the zinc structure to 2.26 Å in (FeL)$_2$ is accompanied by a corresponding decrease in the nitrogen–metal–nitrogen angle from 87.0 to 79.2°. This result is consistent with the calculation of Gollogly and Hawkins[22,23c] on ethylenediamine chelate rings.

A similar effect is observed for the C–N–metal–S–C chelate rings, for as the metal–nitrogen and metal–sulfur distances increase, the intra-ring nitrogen–metal–sulfur angle decreases from 91.7° (av) in the zinc structure to the value of 83.7° (av) in both (FeL)$_2$ and (FeL′)$_2$.

The idealized coordination geometry requires the bond angles around the metal ion to be 109.5° in the case of the tetrahedron and 90, 120, or 180° in the case of the trigonal bipyramid. It is obvious that for complexes of L or L′, the intra-ring ligand–metal–ligand angles prefer to be 95° or less, thus requiring the chelate rings of these ligands to span axial–equatorial bonds in the trigonal bipyramidal coordination geometry. Constraint of the intra-ring angle to values less than 90° in the trigonal bipyramid and 109.5° in the tetrahedron produces strain.

For the sake of discussion, the strain in the complexes will be defined as the deviation of the observed intra-chelate ring angle from the corresponding value in an idealized polyhedron divided by the idealized angle. In the zinc complex,[6] all three intra-ring angles (S1–Zn–N2 = 91.6°, N1–Zn–N2 = 87.0°, S2–Zn–N1 = 91.8°) are smaller than 109.5°. Here the accumulated strain is enormous (−16.3, −20.5, and −16.2%, respectively), causing a folding of the two C–N–Zn–S–C rings back toward the N1–Zn1–N2 plane (see Figure 1, ref 6) and an opening of the inter-ring angle S1–Zn1–S2 to a very large value of 148.1°. The dihedral angle between planes S1–Zn1–S2 and N1–Zn1–N2 is reduced to a value of 75.2°, which is

15° smaller than the value expected for a regular tetrahedron.

In (FeL')₂ the angle N1–Fe–N2 of 90.3° is almost exactly the value corresponding to the idealized trigonal bipyramidal coordination. In the idealized geometry, the S1 atom would be on the plane formed by the Fe, N1, and N2 atoms; in (FeL')₂, S1 is only 0.232(2) Å from that plane and the dihedral angle between the S1–Fe–N1 and the N1–Fe–N2 planes is only 5.4°. Comparing (FeL)₂ with (FeL')₂, one can see that the small N1–Fe–N2 angle of 79.2° in (FeL)₂ required by its five-membered diamine ring conformation has induced strain ($-12.0\%$) which (i) opens up the S1–Fe–S1' angle from 93.09 (8) to 97.3 (2)° and (ii) twists the S1–Fe–N1 plane away from the N1–Fe–N2 plane to produce a dihedral angle of 14.5° between these two planes.

Choosing N1–Fe–N2 as the reference plane, moving N1 toward N2 by 11° in going from (FeL')₂ to (FeL)₂ causes a pulling force on the S1 atom. In order to maintain constant iron–sulfur distances (bond lengths generally being energetically more difficult to distort than interbond angles), the S1–Fe–S1' angle opens with the result that the two iron atoms are drawn closer to one another. Moreover, instead of moving the S1 atom on the N1–Fe–N2 plane to reach the required S1–Fe–N1 angle with a resultant large increase in the S1–Fe–S1' angle, a twisting of the S1–Fe–N1 plane toward the N1–Fe–N2 plane also occurs to help release the strain on the N2–N1–S1 ligand chain.

The net result is to deform the Fe₂S₂ bridging plane and to alter the Fe–S1–Fe' angle from 86.91 (8)° in (FeL')₂ to a more acute value of 82.7 (2)° in (FeL)₂. The nonbonded iron–iron distance is shortened significantly from 3.371 (2) to 3.206 (5) Å (Table VIII). The iron atom is pulled toward the S1 atom and now lies 0.107 (3) Å out of the N1–S1'–S2 equatorial plane.

In summary, the geometries of the three complexes [Zn₂LCl₂]₂, (FeL)₂, and (FeL')₂ may be rationalized as follows.

(1) Given that the metal–ligand bond lengths are determined by the covalent radii of the donor and metal atoms, the intrachelate bond angles are fixed according to the size of the chelate ring.[23,24]

(2) The chelate rings adapt to the coordination geom-etry if possible (e.g., a five-membered ring does not span a set of equatorial bonds in the trigonal bipyramid).

(3) The consequences of any strain, defined as the ratio of the deviation from ideality of the angle determined in (1) divided by the idealized angle, are manifest as distortions in extrachelate coordination bond angles and/or by distortions of the coordination polyhedron from the idealized geometry. In the case of the binuclear complex (FeL)₂, the distortion results in a shorter nonbonded Fe···Fe contact in the plane of Fe₂S₂ rhombus, as discussed above.

## Concluding Remarks

As shown here, the metal–metal distance in binuclear Fe₂(SR)₂ complexes is sensitive to external ligand constraints. We were particularly interested to demonstrate this point in a small molecule since it has been suggested[4,25] that the different protein conformations of the Fe₂S₂* proteins (plant ferredoxins, adrenodoxin, putidaredoxin) resulting from their different amino acid sequences might distort the iron–sulfur core geometries producing the observed differences in their physical properties.[26] Temperature-dependent magnetic susceptibility studies reveal substantially stronger metal–bridge–metal antiferromagnetic coupling in (FeL)₂ than in (FeL')₂.[7] Further chemical and physical studies of these compounds are in progress.

**Supplementary Material Available.** A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $4.00 for photocopy or $2.00 for microfiche, referring to code number JACS-74-2366.

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