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The Crystal Structure of Bis(imidotetramethyldithiodiphosphino-*S*,*S*)iron(II), a Complex with a Tetrahedral FeS_4 Core

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Received December 9, 1970

Bis(imidotetramethyldithiodiphosphino-*S*,*S*)iron(II), $[SP(CH_3)_2NP(CH_3)_2S]_2Fe^{II}$, crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ (C_{2h}^5; no. 14) with a = 9.303 (10), b = 14.186 (10), c = 16.271 (18) Å, β = 101.65 (8)°, and V = 2103 Å^3. Observed and calculated densities are, respectively, ρ_{obsd} = 1.46 (3) and ρ_{calcd} = 1.441 g cm^{-3} for Z = 4. The complex is *not* isomorphous with the corresponding Ni(II) and Co(II) species. Diffraction data to sin θ = 0.36 (Mo Kα radiation) were collected with a 0.01°-incrementing Supper-Pace diffractometer, and the structure was solved by a combination of Patterson, Fourier, and least-squares refinement techniques. All nonhydrogen atoms have been located, the final discrepancy index being R_F = 5.98% for the 1811 independent, nonzero reflections. The crystal consists of discrete molecular units of $[SP(CH_3)_2NP(CH_3)_2S]_2Fe^{II}$, separated by normal van der Waals distances. The central iron atom is *tetrahedrally* coordinated by four sulfur atoms; Fe–S bond distances range from 2.339 (3) to 2.380 (3) Å; S–Fe–S bond angles vary from 100.5 (1) to 114.9 (1)°. The molecule may be useful as a structural model for the nonhaeme iron protein, rubredoxin.

Introduction

The synthesis of the complexes $[SP(CH_3)_2NP(CH_3)_2S]_2M^{II}$ (M = Fe, Co, Ni) has recently been reported.[2] The Ni(II) complex is the sole example of a tetrahedral NiS_4 species.[3,4] The Co(II) species has been shown to be isomorphous with the Ni(II) complex;[5] the Fe(II) complex, however, is not isomorphous with the corresponding Ni(II) and Co(II) derivatives.[6]

A knowledge of the molecular geometry of $[SP(CH_3)_2NP(CH_3)_2S]_2Fe^{II}$ is important for the following reasons. (i) No unambiguous example has been reported previously of a simple Fe(II) complex tetrahedrally coordinated to four sulfur atoms. Thus, the claimed preparation of $[SC(CH_3)CHC(CH_3)S]_2Fe^{II}$[7] has been found to be irreproducible,[8] and only magnetic and spectral data are available for the species $(F_2PS_2)_2Fe^{II}$[9] and $[(CH_3)_3AsS]_4(Fe^{II})^{2+}$.[10]

(ii) Crystallographic studies[11-14] have shown that rubredoxin, a nonhaeme iron protein (mol wt ~6300) from *Clostridium pasteurianum*, contains a single iron atom which is in "highly distorted tetrahedral" coordination to four sulfur atoms. The overall molecular geometry of the protein does not change significantly from the oxidized red form [possibly Fe(III)] to the reduced colorless form [Fe(II)].

The present $[SP(CH_3)_2NP(CH_3)_2S]_2Fe^{II}$ molecule may thus be of some utility as a structural model for the FeS_4 core of rubredoxin, and perhaps, even, for the iron–sulfur center of certain ferredoxins. We have therefore undertaken a single-crystal X-ray diffraction study of $[SP(CH_3)_2NP(CH_3)_2S]_2Fe^{II}$. A preliminary account of this work has appeared previously.[6]

Unit Cell and Space Group

Crystals of $[SP(CH_3)_2NP(CH_3)_2S]_2Fe^{II}$ were supplied by Professor A. Davison and Mrs. E. S. Switkes of the Massachusetts Institute of Technology.

Optical examination and the observed reciprocal lattice symmetry of $2/m$ (C_{2h}) indicated that the crystals belong to the monoclinic system. A careful survey of $h(0\text{–}1)l$, $(0\text{–}1)kl$, and $hk(0\text{–}1)$ Weissenberg and precession photographs revealed the systematic absences $0k0$ for $k = 2n + 1$ and $h0l$ for $l = 2n + 1$, uniquely determining the space group as $P2_1/c$ (C_{2h}^5; no. 14).[15]

Unit cell dimensions were obtained from high-angle reflections on 25°-precession photographs taken at ambient temperatures (24 ± 2°) with Mo Kα radiation (λ 0.7107 Å) and calibrated with $Pb(NO_3)_2$ (a = 7.8566 Å). They are a = 9.303 (10) Å, b = 14.186 (10) Å, c = 16.271 (18) Å, β = 101.65 (8)°. The unit cell volume is 2103 Å^3.

The observed density (ρ_{obsd} = 1.46 (3) g cm^{-3}; by flotation in bromoform–hexane) is consistent with the value calculated for M = 456.29 and Z = 4 (ρ_{calcd} = 1.441 g cm^{-3}). No crystallographic symmetry is imposed upon the molecule.

Collection and Reduction of X-Ray Diffraction Data

Intensity data were collected using Mo Kα radiation (*i.e.*, molybdenum X-radiation filtered through a 3.0-ml zirconium foil at the source) on a 0.01°-incrementing Supper-Pace "Buerger automated diffractometer." A "stationary-background, ω-scan, stationary-background" counting sequence was used in conjunction with equiinclination Weissenberg geometry. A general account of the experimental technique has appeared previously;[16] details specific to the present study include the

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(15) "International Tables for X-Ray Crystallography," Vol. 1, Kynoch Press, Birmingham, England, 1965, p 99.

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following: (i) generator power 49 kV/19 mA; (ii) angle scanned, $\omega(hkl) = [1.2 + 0.6/L(hkl)]^\circ$, where $1/L(hkl)$ is the Lorentz factor for the reflection *hkl;* the count associated with this scan is $C(hkl)$; (iii) $d\omega/dt = 2.0^\circ/\text{min}$; (iv) initial and final backgrounds, $B_1(hkl)$ and $B_2(hkl)$, were each measured for one-fourth the time of the ω scan; (v) a strong preselected check reflection was measured after each 20 reflections within a given zone; no deviations >2% from the mean were observed; (vi) the integrated intensity was calculated as $I(hkl) = C(hkl) - 2.0[B_1(hkl) + B_2(hkl)]$.

Based on previous experience with the ω-scan technique, data were assigned the following standard deviations: $I(hkl) \geqslant 4900$, $\sigma\{I(hkl)\} = 0.1[I(hkl)]$; $4900 \geqslant I(hkl) \geqslant \{3.0[C(hkl) + 4B_1(hkl) + 4B_2(hkl)]^{1/2}\}$, $\sigma\{I(hkl)\} = 7.0[I(hkl)]^{1/2}$; $\{3.0[C(hkl) + 4B_1(hkl) + 4B_2(hkl)]^{1/2}\} > I(hkl)$, $\sigma\{I(hkl)\} = -1.0[I(hkl)]$. This last condition removes all reflections which are not significantly (3σ) above background.

Two crystals were used in data collection. Crystal I ($0.28 \times 0.50 \times 0.29$ mm for $\vec{a}, \vec{b}, \vec{c}$) was mounted on its b axis and used in collecting data for the quadrants hkl and $hk\bar{l}$ of levels $h(0\text{–}14)l$; this set of data is complete to $\sin\theta = 0.36$ save for reflections with $\theta \leqslant 4^\circ$ which are shielded from the scintillation counter by a lead backstop. Crystal II ($0.44 \times 0.55 \times 0.40$ mm for $\vec{a}, \vec{b}, \vec{c}$) was mounted on its a axis and used in collecting correlation data from quadrants hkl and $hk\bar{l}$ of levels $hk(0\text{–}2)$. Of 2373 reflections collected from crystal I, 511 were not significantly above background; for crystal II the appropriate figures are 1045 and 211, respectively. All intensities were now corrected for Lorentz, polarization, and absorption effects.[17] With $\mu = 14.05$ cm^{-1} transmission factors ranged 0.700–0.791 for crystal I (volume 0.0172 mm^3) and 0.606–0.641 for crystal II (volume 0.0457 mm^3). Equivalent reflections (*e.g.*, $0kl$, $0k\bar{l}$) were averaged within each zone; the 18 levels were then merged to a common scale by a least-squares analysis of common reflections.[18] The "R factor" for scaling was 5.77%, based on F^2. The resulting 1811 independent nonzero reflections were placed on an approximate absolute scale by means of a Wilson plot,[19] which also suggested an overall isotropic thermal parameter of $B = 2.11$ Å^2.

Elucidation and Refinement of the Structure

Unless otherwise stated, calculations were performed on the Harvard University IBM 7094 computer using the CRYRM system.[20] Scattering factors for neutral iron, sulfur, phosphorus, nitrogen, and carbon were taken from the compilation of Ibers.[21] A correction was made for the *real* part of the dispersion (*viz.*, $\Delta f'(\text{Fe}) = +0.4\,e^-$, $\Delta f'(\text{S}) = +0.1\,e^-$, $\Delta f'(\text{P}) = +0.1\,e^-$), but not for the imaginary components.

The residual minimized during least-squares refinement was $\Sigma w(|F_o|^2 - |F_c|^2)^2$ where $w(hkl) = [\sigma\{F^2(hkl)\}]^{-2}$ and $\sigma\{F^2(hkl)\}$ is derived from $\sigma I\{(hkl)\}$ by appropriate adjustment for Lorentz, polarization, transmission, and scale factors. Discrepancy indices used below are $R_F = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_{wF^2} = \Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w|F_o|^4$.

The positions of the iron, four sulfur, and four phosphorus atoms were determined from a three-dimensional Patterson map which had been "sharpened" such that the average intensity was no longer θ dependent. A difference-Fourier synthesis, phased by the nine "heavy" atoms ($R_F = 32.3\%$), revealed the positions of nitrogen and carbon atoms. Four cycles of full-matrix refinement of positional and isotropic thermal parameters led to convergence at $R_F = 9.65\%$, $R_{wF^2} = 5.40\%$. A further three cycles of refinement, now using anisotropic thermal parameters for the 19 nonhydrogen atoms, resulted in convergence at $R_F = 6.22\%$, $R_{wF^2} = 2.55\%$. Another three cycles of anisotropic refinement, now including a secondary extinction correction, gave convergence $[(\Delta/\sigma)_{\max} < 0.01]$ at $R_F = 5.98\%$, $R_{wF^2} = 2.47\%$. The final value of the secondary extinction coefficient (based on the model of Zachariasen[22]) was $X = 1.48 \times 10^{-6}$, where $F_c^2(\text{cor}) = F_c^2(\text{uncor})/[1 + X\beta F_c^2(\text{uncor})]$ and $\beta = (1 + \cos^4 2\theta)/[\sin\theta(1 + \cos^2 2\theta)]$.

The hydrogen atoms of the eight methyl groups could not be located at any stage of the refinement process; a final difference-Fourier map showed no features higher than 0.4 e$^-$ Å^{-3} and the structure was judged to be correct and complete. The standard deviation in a reflection of unit weight was 1.37.

Hamilton R factor ratio tests[23] justify as significant improvements (i) refinement of anisotropic thermal parameters and (ii) inclusion of a secondary extinction factor.

A table of observed and calculated structure factors has been deposited.[24] Final atomic coordinates are collected in Table I. Anisotropic thermal parameters are shown in Table II; their associated thermal vibration ellipsoids are listed in Table III and are displayed pictorially[25] in Figure 1.

TABLE I

FINAL ATOMIC COORDINATES FOR $[SP(CH_3)_2NP(CH_3)_2S]_2Fe^{II}$, WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Atom	x	y	z
Fe	0.27135 (18)	0.21114 (9)	0.28056 (9)
S(1)	0.01857 (34)	0.23102 (18)	0.27672 (18)
S(2)	0.30876 (36)	0.15359 (20)	0.15012 (18)
S(3)	0.35552 (35)	0.36472 (17)	0.31301 (20)
S(4)	0.35230 (39)	0.10394 (20)	0.39298 (19)
P(1)	−0.06621 (33)	0.12750 (17)	0.19576 (16)
P(2)	0.10929 (37)	0.17498 (19)	0.07485 (18)
P(3)	0.56964 (35)	0.33425 (17)	0.35099 (18)
P(4)	0.56582 (35)	0.14196 (17)	0.41827 (16)
N(1)	−0.0316 (11)	0.1333 (6)	0.1030 (5)
N(2)	0.6092 (11)	0.2257 (5)	0.3634 (5)
C(1)	−0.2610 (13)	0.1292 (7)	0.1853 (7)
C(2)	−0.0066 (14)	0.0133 (7)	0.2426 (7)
C(3)	0.0902 (16)	0.3023 (8)	0.0557 (9)
C(4)	0.1126 (15)	0.1230 (9)	−0.0253 (7)
C(5)	0.6652 (17)	0.3794 (7)	0.2750 (9)
C(6)	0.6305 (18)	0.4015 (8)	0.4463 (8)
C(7)	0.6788 (16)	0.0427 (6)	0.4011 (8)
C(8)	0.6162 (15)	0.1649 (8)	0.5292 (7)

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[17] Using the IBM 360 program IMBIBE, written by J. Wormald.

[18] A. D. Rae, *Acta Crystallogr.*, **19**, 683 (1965).

[19] A. J. C. Wilson, *Nature (London)*, **150**, 152 (1942).

[20] CRYRM is an integrated sequence of crystallographic routines for the IBM 7094, written by Dr. R. E. Marsh and coworkers at the California Institute of Technology.

[21] "International Tables for X-Ray Crystallography," Vol. 3, Kynoch Press, Birmingham, England, 1962: (a) pp 202–207; (b) p 216.

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[24] Document No. NAPS-01400, National Auxiliary Publication Service, c/o CCM Information Corp., 909 3rd Ave., New York, N. Y. 10022. A copy may be secured by citing the document number and remitting $5.50 for photocopies or $2.00 for microfiche. Advance payment is required. Make checks or money order payable to CCMIC–NAPS.

[25] Using OTLIPS, an IBM 1620/CALCOMP-plotter program written by Dr. P. H. Bird.

TABLE II

ANISOTROPIC THERMAL PARAMETERS[a] (×10⁴), FOR $[SP(CH_3)_2NP(CH_3)_2S]_2Fe^{II}$, WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Fe	87.7 (2.8)	37.2 (0.8)	30.5 (0.8)	−4.0 (2.2)	12.6 (2.2)	−2.7 (1.1)
S(1)	84.3 (4.9)	50.4 (1.6)	45.3 (1.5)	−7.8 (4.5)	25.2 (4.5)	−37.6 (2.4)
S(2)	96.8 (5.4)	62.3 (1.8)	37.8 (1.5)	14.2 (4.8)	34.0 (4.6)	−16.2 (2.5)
S(3)	81.1 (5.0)	32.2 (1.4)	65.2 (1.9)	9.4 (4.1)	19.8 (5.0)	−8.2 (2.4)
S(4)	125.3 (5.7)	58.4 (1.7)	44.2 (1.6)	−50.1 (4.9)	−0.3 (4.9)	34.3 (2.5)
P(1)	71.4 (4.7)	38.2 (1.4)	24.0 (1.3)	−8.8 (4.0)	20.1 (3.9)	−0.3 (2.0)
P(2)	96.4 (5.2)	47.1 (1.5)	29.8 (1.4)	−10.4 (4.7)	34.8 (4.3)	6.2 (2.3)
P(3)	83.3 (5.0)	34.5 (1.4)	34.8 (1.4)	−8.1 (4.2)	17.3 (4.2)	7.2 (2.2)
P(4)	103.5 (5.2)	32.6 (1.4)	27.0 (1.3)	7.1 (4.2)	25.8 (4.2)	7.9 (2.0)
N(1)	126 (18)	81 (6)	32 (5)	−82 (17)	50 (15)	−22 (9)
N(2)	126 (17)	32 (4)	45 (5)	38 (4)	64 (15)	16 (7)
C(1)	77 (20)	57 (6)	44 (6)	5 (18)	22 (18)	7 (10)
C(2)	142 (22)	29 (5)	55 (6)	3 (17)	25 (19)	2 (9)
C(3)	177 (28)	56 (7)	86 (9)	48 (22)	77 (26)	48 (12)
C(4)	110 (22)	116 (10)	28 (5)	−8 (24)	33 (18)	−11 (11)
C(5)	234 (32)	44 (6)	110 (10)	41 (21)	243 (31)	59 (12)
C(6)	247 (33)	52 (7)	59 (7)	−19 (23)	−116 (25)	−20 (11)
C(7)	230 (28)	27 (5)	64 (7)	76 (18)	103 (23)	28 (9)
C(8)	158 (25)	72 (7)	31 (5)	−4 (22)	−22 (9)	−10 (10)

[a] The anisotropic thermal parameter is defined as $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

TABLE III

ROOT-MEAN-SQUARE AMPLITUDES OF VIBRATION (IN Å) ALONG THE PRINCIPAL AXES OF THE ATOMIC VIBRATION ELLIPSOIDS[a]

Atom	$[\overline{U^2}_{max}]^{1/2}$	$[\overline{U^2}_{med}]^{1/2}$	$[\overline{U^2}_{min}]^{1/2}$
Fe	0.205	0.197	0.185
S(1)	0.277	0.188	0.182
S(2)	0.262	0.218	0.188
S(3)	0.294	0.191	0.173
S(4)	0.305	0.213	0.188
P(1)	0.199	0.177	0.168
P(2)	0.223	0.209	0.177
P(3)	0.218	0.191	0.178
P(4)	0.211	0.193	0.171
N(1)	0.316	0.199	0.183
N(2)	0.266	0.201	0.165
C(1)	0.247	0.232	0.179
C(2)	0.271	0.243	0.173
C(3)	0.352	0.266	0.208
C(4)	0.345	0.216	0.184
C(5)	0.431	0.217	0.159
C(6)	0.409	0.243	0.177
C(7)	0.340	0.251	0.137
C(8)	0.285	0.271	0.179

[a] The orientation of the atomic vibration ellipsoids is illustrated in Figure 1.

TABLE IV

INTERATOMIC DISTANCES (Å) FOR $[SP(CH_3)_2NP(CH_3)_2S]_2Fe^{II}$ WITH ESTIMATED STANDARD DEVIATIONS[a,b]

Atom	Dist	Atom	Dist
Fe–S(1)	2.356 (3)	Fe–S(3)	2.339 (3)
Fe–S(2)	2.364 (3)	Fe–S(4)	2.380 (3)
S(1)–P(1)	2.023 (3)	S(3)–P(3)	2.009 (4)
S(2)–P(2)	2.029 (4)	S(4)–P(4)	2.019 (4)
P(1)–N(1)	1.608 (9)	P(3)–N(2)	1.586 (8)
P(2)–N(1)	1.586 (9)	P(4)–N(2)	1.585 (8)
P(1)–C(1)	1.786 (11)	P(3)–C(5)	1.781 (14)
P(1)–C(2)	1.827 (11)	P(3)–C(6)	1.812 (14)
P(2)–C(3)	1.835 (14)	P(4)–C(7)	1.812 (12)
P(2)–C(4)	1.794 (13)	P(4)–C(8)	1.801 (12)

[a] Esd's for individual bond lengths (and bond angles) are obtained from the least-squares refinement process *via* the inverse matrix. [b] Average values are collected in Table VII.

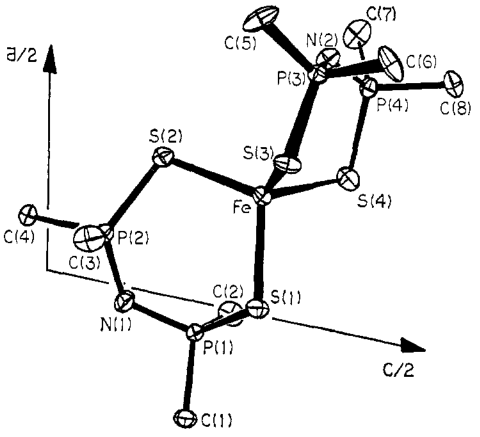

Figure 1.—Atomic numbering and thermal vibration ellipsoids for $[SP(CH_3)_2NP(CH_3)_2S]_2Fe^{II}$, viewed down *b* (OTLIPS diagram[25]).

TABLE V

BOND ANGLES (DEG) FOR $[SP(CH_3)_2NP(CH_3)_2S]_2Fe^{II}$ WITH ESTIMATED STANDARD DEVIATIONS[a]

Atoms	Angle	Atoms	Angle
S(1)–Fe–S(2)	110.1 (0.1)	S(2)–Fe–S(3)	114.9 (0.1)
S(1)–Fe–S(3)	100.5 (0.1)	S(2)–Fe–S(4)	112.8 (0.1)
S(1)–Fe–S(4)	104.8 (0.1)	S(3)–Fe–S(4)	112.4 (0.1)
Fe–S(1)–P(1)	100.7 (0.1)	Fe–S(3)–P(3)	97.8 (0.1)
Fe–S(2)–P(2)	102.0 (0.2)	Fe–S(4)–P(4)	97.6 (0.2)
S(1)–P(1)–N(1)	116.6 (0.4)	S(3)–P(3)–N(2)	115.9 (0.4)
S(2)–P(2)–N(1)	118.6 (0.4)	S(4)–P(4)–N(2)	115.9 (0.4)
P(1)–N(1)–P(2)	128.6 (0.6)	P(3)–N(2)–P(4)	136.1 (0.6)
S(1)–P(1)–C(1)	107.9 (0.4)	S(3)–P(3)–C(5)	108.2 (0.5)
S(1)–P(1)–C(2)	109.0 (0.4)	S(3)–P(3)–C(6)	105.6 (0.5)
S(2)–P(2)–C(3)	107.1 (0.5)	S(4)–P(4)–C(7)	109.8 (0.4)
S(2)–P(2)–C(4)	107.8 (0.4)	S(4)–P(4)–C(8)	107.4 (0.4)
N(1)–P(1)–C(1)	107.5 (0.5)	N(2)–P(3)–C(5)	105.9 (0.5)
N(1)–P(1)–C(2)	109.6 (0.5)	N(2)–P(3)–C(6)	112.6 (0.5)
N(1)–P(2)–C(3)	111.0 (0.6)	N(2)–P(4)–C(7)	107.6 (0.6)
N(1)–P(2)–C(4)	105.9 (0.6)	N(2)–P(4)–C(8)	112.2 (0.6)
C(1)–P(1)–C(2)	105.6 (0.5)	C(5)–P(3)–C(6)	107.0 (0.6)
C(3)–P(2)–C(4)	105.6 (0.6)	C(7)–P(4)–C(8)	104.7 (0.6)

[a] See footnotes to Table IV.

The Molecular Structure

Interatomic distances with estimated standard deviations (esd's) are given in Table IV; bond angles, with esd's, are shown in Table V. The important molecular planes are defined in Table VI.

The $[SP(CH_3)_2NP(CH_3)_2S]_2Fe^{II}$ molecule contains an iron(II) center which is in tetrahedral coordination to four sulfur atoms. This is as predicted by Davison and Switkes[2] from magnetic and spectral data on this

TABLE VI
LEAST-SQUARES PLANES IN THE
$[SP(CH_3)_2NP(CH_3)_2S]_2Fe^{II}$ MOLECULE[a-c]

Atom	Dev, Å	Atom	Dev, Å
(a) $0.1216X + 0.9385Y - 0.3233Z - 1.561 = 0$			
Fe*	0.0	N(1)	−0.393 (10)
S(1)*	0.0	C(1)	−1.164 (11)
S(2)*	0.0	C(2)	−2.738 (12)
P(1)	−1.025 (3)	C(3)	+2.256 (13)
P(2)	+0.477 (3)	C(4)	+0.344 (12)
(b) $-0.9110X + 0.1969Y + 0.3620Z - 0.749 = 0$			
Fe*	0.0	N(2)	−2.096 (10)
S(3)*	0.0	C(5)	−2.917 (13)
S(4)*	0.0	C(6)	−1.059 (13)
P(3)	−1.567 (3)	C(7)	−2.867 (12)
P(4)	−1.482 (3)	C(8)	−0.872 (12)

[a] Planes are defined in Cartesian coordinates (X, Y, Z), which are related to the monoclinic fractional cell coordinates (x, y, z) by the transformations $X = xa + zc \cos \beta$, $Y = yb$, and $Z = zc \sin \beta$. [b] Planes are calculated using unit weights for all atoms marked with an asterisk. [c] The interplanar angle is 87.5°.

complex, *i.e.*, magnetic moment 5.25 BM in the solid state and 4.99 BM in CH_2Cl_2 solution (*cf.* 4.90 BM predicted as the spin-only value for an $e^3t_2^3$ electronic configuration); the optical spectrum contains three bands, λ_{max} 3100, 4098, 5000 cm^{-1} with ϵ 101, 108, ~70 l. mol^{-1} cm^{-1}, respectively.

Iron–sulfur bond lengths in the molecule range from Fe–S(3) = 2.339 (3) Å to Fe–S(4) = 2.380 (3) Å, averaging 2.360 (17) Å. The FeS_4 coordination tetrahedron is slightly irregular, *intra*ligand angles being S(1)–Fe–S(2) = 110.1 (0.1)° and S(3)–Fe–S(4) = 112.4 (0.1)°. The dihedral angle between these two S–Fe–S planes is 87.5° (see Table VI). However, the distortion of the central FeS_4 moiety from a regular tetrahedral arrangement cannot be described as a simple twist of one chelate ring away from orthogonality to the other (*i.e.*, distortion toward planarity with symmetry being lowered from T_d to D_2). Rather, the distortion is equivalent to a slight rotation [toward S(1)] of the S(3)–Fe–S(4) system, about an axis passing through the iron atom and lying essentially perpendicular to the S(1)–Fe–S(2) plane. Thus, *inter*ligand angles from S(1) are each lower than expected [*i.e.*, S(1)–Fe–S(3) = 100.5 (0.1)° and S(1)–Fe–S(4) = 104.8 (0.1)°] while angles from S(2) are each increased from the ideal tetrahedral value [*viz.*, S(2)–Fe–S(3) = 114.0 (0.1)° and S(2)–Fe–S(4) = 112.8 (0.1)°].

Although a tetrahedral d^6 complex has a degenerate ground state (*i.e.*, $e^3t_2^3$), this degeneracy occurs in the nonbonding e electrons and not in the antibonding t_2 level. No appreciable Jahn–Teller[26] distortion is expected. The observed angular distortions are thus, presumably, the result of intermolecular interactions. [However, these cannot be specified, since hydrogen atoms were not located.]

As can be seen from Table VII, the average bond distances within the imidotetramethyldithiodiphosphinate ligands [*i.e.*, S–P = 2.020 (8), P–N = 1.591 (11), and P–C = 1.806 (19) Å] are in good agreement with values obtained from our previous structural study of $[SP(CH_3)_2NP(CH_3)_2S]_2Ni^{II}$.[3,4] Although the present Fe(II) complex and the Ni(II) complex are not isomorphous, there are certain similarities in their overall molecular conformations.

TABLE VII
COMPARISON OF DIMENSIONS WITHIN
$[SP(CH_3)_2NP(CH_3)_2S]_2M$ COMPLEXES

	M = Fe(II)	M = Ni(II)
I. Average Bond Lengths,[a] Å		
M–S	2.360 (17)[b]	2.282 (12)[b]
S–P	2.020 (8)	2.023 (6)
P–N	1.591 (11)	1.580 (7)
$P-CH_3$	1.806 (19)	1.825 (25)
II. Average Bond Angles,[a] Deg		
S–M–S	109.3 (5.5)[b]	109.5 (4.1)[b]
M–S–P	99.5 (2.2)	104.6 (1.4)
S–P–N	116.7 (1.3)	116.6 (0.8)
P–N–P	132.3 (5.3)[b]	128.4 (0.9)
$S-P-CH_3$	107.9 (1.3)	107.6 (2.1)
$N-P-CH_3$	109.0 (2.7)	108.6 (1.7)
CH_3-P-CH_3	105.7 (0.8)	107.2 (1.9)
III. Conformation of Chelate Rings		
(a) Deviations from S(1)–M–S(2) Plane, Å		
C(1)	−1.164	−1.170
C(2)	−2.738	−2.807
P(1)	−1.025	−1.081
N(1)	−0.393	−0.527
P(2)	+0.477	+0.422
C(3)	+2.256	+2.165
C(4)	+0.344	+0.225
(b) Deviations from S(3)–M–S(4) Plane, Å		
C(5)	−2.917	−3.094
C(6)	−1.059	−1.149
P(3)	−1.567	−1.414
N(2)	−2.096	−1.433
P(4)	−1.482	−0.356
C(7)	−2.867	−0.945
C(8)	−0.872	+1.272

[a] Esd's for average bond lengths and angles are calculated from the equation

$$\sigma = \left\{ \sum_{i=1}^{N} (\chi_i - \bar{\chi})^2/(N - 1) \right\}^{1/2}$$

where χ_i is length of ith bond and $\bar{\chi}$ is the mean value for the N equivalent bond lengths. [b] The relatively large esd's on these mean values (as compared to esd's on the individual bonds or angles) lead us to believe that these bond lengths (or bond angles) are *not* chemically equivalent—see text and ref 4.

Thus, deviations of atoms from the S(1)–M–S(2) planes (M = Fe, Ni) are closely similar in the two cases, indicating that these chelate rings have the same conformation (see Table VII). Moreover, the C(5)–P(3)–C(6) systems have essentially the same relationship to their appropriate S(3)–M–S(4) planes. Thus, the only major conformational difference between the solid-state molecular structure of $[SP(CH_3)_2NP(CH_3)_2S]_2Fe^{II}$ and that of $[SP(CH_3)_2NP(CH_3)_2S]_2Ni^{II}$ involves the disposition of atoms N(2), P(4), C(7), and C(8). While there is no simple description for the conformation of the Ni–S(3)–P(3)–N(2)–P(4)–S(4) ring, the corresponding ring in the Fe(II) complex clearly takes up a boat conformation, with Fe and N(2) as the apices (see Figure 1).

It is interesting to note that, while individual P–N–P bond angles are 127.7 (0.6) and 129.0 (0.6)° in the Ni(II) complex and the P(1)–N(1)–P(2) angle is 128.6 (0.6)° in the present Fe(II) complex, the P(3)–N(2)–P(4) angle in the Fe(II) complex is expanded to 136.1 (0.6)°. This is clearly of statistical significance (an increase of 7.5° represents approximately 12 standard deviations). We believe that it results from intramolecular interactions within the chelate ring caused by

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[26] H. A. Jahn and E. Teller, *Proc. Roy Soc., Ser. A*, **161**, 220 (1937).

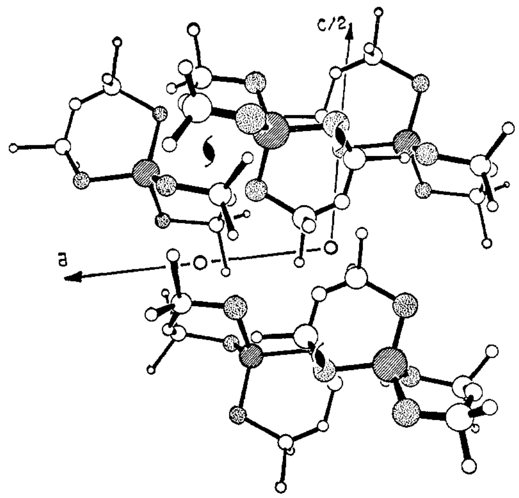

Figure 2.—Packing of $[SP(CH_3)_2NP(CH_3)_2S]_2Fe^{II}$ molecules in the unit cell.

the energetically unfavorable boat conformation. In particular, we suspect that there are interactions between hydrogen atoms associated with the CH_3(axial) $\cdots CH_3$(axial) contact, $C(6)\cdots C(8) = 3.629\ (13)$ Å (see Figure 1). [The CH_3(eq)$\cdots CH_3$(eq) contact, $C(5)\cdots C(7)$, is 5.192 (14) Å.]

All other features of the structure of $[SP(CH_3)_2NP(CH_3)_2S]_2Fe^{II}$ closely resemble those found in the analogous Ni(II) species.[3,4]

In summary, $[SP(CH_3)_2NP(CH_3)_2S]_2Fe^{II}$ is the first confirmed example of a simple tetrahedral complex with an FeS_4 core. There is no ready explanation as to why the Fe(II) center has a tetrahedral (rather than square planar) coordination sphere, except that it may be noted that an S–Fe–S angle of 109° 28′ affords a more strain-free ligand geometry than would the square-planar angle of 90°.

The Crystal Structure

No intermolecular contacts of less than 3.5 Å were found. [This does not, however, include those involving hydrogen atoms, which were not detected in this analysis.] It is, nevertheless, clear that the crystal consists of independent molecular units of $[SP(CH_3)_2NP(CH_3)_2S]_2Fe^{II}$, held apart by normal van der Waals forces. The packing of molecules within the unit cell is illustrated in Figure 2.

Acknowledgments.—We thank Professor A. Davison and Mrs. E. S. Switkes for supplying samples of the title complex. This work was supported by the Advanced Research Projects Agency and the National Science Foundation (GP-26293). J. W. gratefully acknowledges receipt of a Graduate National Fellowship from Harvard University for 1967–1970.

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The Crystal and Molecular Structure of Racemic (4-(2-Aminoethyl)-1,4,7,10-tetraazadecane)azidocobalt(III) Nitrate Hydrate

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Received February 9, 1970

The crystal and molecular structure of racemic (4-(2-aminoethyl)-1,4,7,10-tetraazadecane)azidocobalt(III) nitrate hydrate, *sym*-$[Co(trenen)N_3](NO_3)_2\cdot H_2O$, has been determined from three-dimensional X-ray data collected by counter methods. The compound crystallizes in space group $P2_1/c$ (C_{2h}^5; no. 14), with $a = 8.32$ (1) Å, $b = 7.64$ (1) Å, $c = 27.69$ (3) Å, $\beta = 96.3$ (3)°, and $Z = 4$. Measured and calculated densities are 1.66 (2) and 1.64 (1) g cm^{-3}. Full-matrix least-squares techniques were used to refine the structure to a final residual $R = 0.068$ for 2030 independent nonzero reflections. The crystal is composed of *sym*-$Co(trenen)N_3^{2+}$ cations, NO_3^- anions, and water molecules which are held together by electrostatic forces and hydrogen bonds. The coordination at the metal ion is octahedral with the polyamine ligand coordinated quinquedentate and the azide ion occupying the remaining coordination site. The bifurcated structure of the ligand, trenen, and the mode of coordination have been determined. Ligand chelate ring conformations and the bonding requirements of the azide ion are discussed. Also the relationship between the structure of *sym*-$Co(trenen)N_3^{2+}$ and the base hydrolysis studies of the related chloro complex are discussed.

Introduction

As part of a general study on the stereochemistry and mechanisms of hydrolysis of complexes of the type CoN_5X^{2+} (where N_5 is a multidentate amine, a monodentate amine, ammonia, or a combination, and X is an acido group), four $Co(tetraen)X^{2+}$ (tetraen = tetraethylenepentamine) complexes were prepared and characterized.[1] The commercially available linear tetraen (Union Carbide) was known to contain a considerable percentage of some impurity, probably a branched-chain isomer. This posed the problem of deciding not only between topological isomers in the complexes but also between ligand isomers. In view of the very large number of isomeric possibilities, it was very difficult to make unequivocal structural assignments to the isolated complexes.

Detailed structural knowledge is essential to any comprehensive study of the mechanisms of hydrolysis of these compounds. Further, the conformations of the chelate rings in these types of complexes are of interest in determining the factors governing the geometries of multidentate amine complexes. Such information could be provided by a crystal structure analysis and

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[1] P. A. Marzilli, Ph.D. Thesis, Australian National University, 1968.