The question as to where the first Me_2SO molecule binds cannot be resolved. However, for a given set of isomers, higher K_1 values may be associated with a "$Rh_2(O_2CCH_3)_3(PhNOCCH_3)$-like" structure (i.e. a structure in which one axial site has more *N*-phenyl groups around it than the other). In contrast, the isomer having a considerably lower K_1 value may be assumed to have a "more even" distribution of N donor atoms around the two rhodium atoms of the dimer. From this line of reasoning, compounds **4**, **6**, and **7** may be candidates for "$Rh_2(O_2CCH_3)_3$-($PhNOCCH_3$)-like" structures. The crystal structure of compound **7**(Me_2SO) (Figure 3a) supports this argument.

On the basis of ^{13}C NMR, it was suggested that compound **6** may have structure IIIb or IIIc shown in Figure 1. Structure IIIc, which has one axial site crowded as in compound **7** (see Figure 3a), will not bind a second Me_2SO molecule. This argues against structure IIIc. Therefore, it is more likely that compound **6** has structure IIIb.

Assignment of compounds **3** and **4** is uncertain. On the basis of their log K_1 values compound **4** has structure IIa or IIb while compound **3** has structure IIc or IId. This is because the steric environment of IIa should be the same as that of IIb with one axial site more crowded than the other. In contrast, structures IIc and IId have equal steric hindrance at each axial site. Unfortunately, a further distinction between structures IIa and IIb or IIc and IId cannot be made since IIa, IIc, and IId are all capable of leading to the formation of structure IIIa. Similarly, IIIb can be formed from either structure IIb or IIc.

In summary, this study has shown that the substitution of phenyl for hydrogen on the acetamide nitrogen changes the isomer distribution among the products. This appears to be due to steric factors involved in axial bond formation of the entering ligand. Significant isomer effects are not observed in the redox potentials. A moderate effect is observed in the electronic absorption spectra of the higher substitution products, and this isomer effect is reflected quite strongly in the formation constants for Me_2SO addition. Thus, it appears that steric crowding around the axial site of the two rhodium ions is a dominant factor in determining differences in chemical and structural properties of the geometric isomers.

Acknowledgment. The support of the Robert A. Welch Foundation (K.M.K., Grant E-680; J.L.B., Grant E-918) is gratefully acknowledged. We also wish to acknowledge Dr. James Korp, University of Houston X-ray Crystallography Center, for performing the X-ray analysis.

Supplementary Material Available: Listings of anisotropic thermal parameters and root-mean-square amplitudes of thermal vibration and complete listings of bond lengths and angles (20 pages); listings of observed and calculated structure factors (22 pages). Ordering information is given on any current masthead page.

Contribution from the Departments of Chemistry, Texas A&M University, College Station, Texas 77843,
Universidad de Santiago, Santiago, Chile, and Faculty of Sciences, Universidad de Chile, Santiago, Chile

Characterization of Tetra-, Penta-, and Hexacoordinated High-Spin Iron(II) Complexes with Neutral Monodentate Sulfur Donor Ligands. Crystal and Molecular Structure of $Fe(DMTU)_7(BF_4)_2$ (DMTU = *N*,*N'*-Dimethylthiourea)

J. P. Fackler,*[†] T. Moyer,[†‡] J. A. Costamagna,*[§] R. Latorre,[∥] and J. Granifo[∥⊥]

Received June 12, 1986

New cationic high-spin iron(II) complexes with substituted thioureas and with perchlorate or tetrafluoroborate anions (X) were obtained: $[FeL_6]X_2$ (L = *N*-ethylthiourea, *N*,*N'*-di-*n*-propylthiourea); $[FeL_n](ClO_4)_2$ (L = *N*,*N'*-dimethylthiourea, *N*,*N'*-diethylthiourea; n = 4, 6); $[Fe(DMTU)_n](BF_4)_2$ (DMTU = *N*,*N'*-dimethylthiourea; n = 4, 5, 7). Tetrahedral ($[FeL_4]X_2$), octahedral ($[FeL_6]X_2$, $[Fe(DMTU)_6](BF_4)_2{\cdot}DMTU$), and pentacoordinate ($[Fe(DMTU)_5](BF_4)_2$) structures have been identified by using electronic and Mössbauer spectroscopies and magnetic susceptibility measurements. For the last structure, a square-base-pyramidal symmetry around the iron atom is proposed. The DMTU complexes are the first examples in which a soft sulfur-binding monodentate ligand is found in binary iron complexes with three different arrangements. It was possible to evaluate the distortion in the tetrahedral complexes ($\Delta_T \sim 800$ cm^{-1}) and to correlate the isomer shift with the coordination number: tetracoordinated ~0.9, pentacoordinated ~1.1, hexacoordinated ~1.2 mm s^{-1}. The absorption and the line width values are highly dependent on the temperature and the nature of the substituent. The crystal structure of the complex $[Fe(DMTU)_6](BF_4)_2{\cdot}DMTU$ was determined by heavy-atom methods and refined by least-squares procedures. Crystals are monoclinic, space group $C2/c$, with a = 13.561 (3) Å, b = 24.008 (4) Å, c = 14.290 (4) Å, β = 91.36 (2)°, and Z = 4, and the structure was refined to R = 0.045 for the 3037 independent reflections greater than 3σ.

Introduction

The structure and bonding of Fe–S compounds have been of interest to us for some years.[1-9] The use of Fe–S compounds as models for iron–sulfur proteins has been pursued by many groups for many years.[10-12] Although there has been much work with Fe(III) complexed with dithiocarbamates and thioxanthates,[13-18] there has been relatively little work on Fe(II) in general and Fe(II) complexes with soft, neutral ligands in particular.

There is some indirect structural information obtained from Mössbauer spectroscopy for iron(II) complexes with substituted thioureas. It has been possible to observe considerable distortion in the crystal field symmetry from that expected for regular

---

(1) Fackler, J. P.; Coucouvanis, D. *Proc. Int. Conf. Coord. Chem.*, *9th* **1966**, 300.
(2) Fackler, J. P.; Holah, D. G. *Inorg. Nucl. Chem. Lett.* **1966**, *2*, 251.
(3) Fackler, J. P.; Seidel, W. C. *Inorg. Chem.* **1969**, *8*, 1631.
(4) Fackler, J. P.; Lin, I. J. B.; Andrews, J. *Inorg. Chem.* **1977**, *16*, 450.
(5) Fackler, J. P.; Thompson, L. D., Jr. *Inorg. Chim. Acta* **1981**, *48*, 45. This paper describes refinement procedures used.
(6) Latorre, R.; Abeledo, C.; Costamagna, J.; Frankel, R.; Reiff, W.; Frank, E. *J. Chem. Phys.* **1973**, *59*, 2580.
(7) Latorre, R.; Costamagna, J.; Frank, E.; Abeledo, C.; Frankel, R. *J. Phys. C* **1974**, *12*, C6-635.
(8) Latorre, R.; Costamagna, J.; Frank, E.; Abeledo, C.; Frankel, R. *J. Inorg. Nucl. Chem.* **1979**, *41*, 649.
(9) Latorre, R.; Costamagna, J.; Navia, P. *J. Phys. C* **1976**, *14*, C6-489.
(10) For a review of this subject, see: (a) Malkin, R.; Rabinowitz, S. J. C. *Annu. Rev. Biochem.* **1967**, *36*, 113. (b) Kimura, T. *Struct. Bonding (Berlin)* **1968**, *5*, 1. (c) Tribi, J. C. M.; Woody, R. W. *Coord. Chem. Rev.* **1970**, *5*, 417.

[*] To whom correspondence should be addressed.
[†] Texas A&M University.
[‡] Studies performed at Case Institute of Technology, Cleveland, OH.
[§] Universidad de Santiago.
[∥] Universidad de Chile.
[⊥] Present address: Department of Chemistry, Universidad de La Frontera, Temuco, Chile.

0020-1669/87/1326-0836$01.50/0 © 1987 American Chemical Society

tetrahedral and octahedral environments in these cases.[6-9] The orbital ground state also has been assigned.

The syntheses of new complexes with different substituted thioureas and with tetrafluoroborate and perchlorate were carried out in order to study the influence of the ligand and anion on the structural behavior of these compounds with temperature. In this work new cationic complexes of substituted thioureas of iron(II) with these anions are described. *N,N′*-Dimethylthiourea (DMTU), *N*-ethylthiourea (NETU), *N,N′*-diethylthiourea (DETU), and *N,N′*-di-*n*-propylthiourea (DPTU) complexes of iron(II) were characterized by ultraviolet–visible spectra, magnetic susceptibilities, and Mössbauer spectra at different temperatures. We also discuss here some structural features in terms of parameters obtained from different spectroscopies and develop correlations between them.

The distortion in sulfur complexes of iron(II) with six (or four) sulfur donor atoms is of interest in comparison to present information with other sulfur ligands. In this study, the crystal and molecular structure of iron(II) coordinated to six sulfur atoms also is presented. It is believed that this is the first report for an FeS_6 molecular structure for iron(II).

Experimental Section

Synthesis of FeL_6X_2 (L = NETU, DETU, DMTU, DPTU; X = ClO_4, BF_4), FeL_4X_2 (L = DMTU, DETU; X = ClO_4, BF_4), and $Fe(DMTU)_7(BF_4)_2$. The following general method was used: A stoichiometric quantity of ligand was added to a concentrated solution of iron(II) perchlorate (or tetrafluoroborate) in 1-butanol, with different volumes of solvent according to the ligand solubility. The mixture was heated and stirred until all the ligand dissolved and then was allowed to stand at 5 °C until crystals were formed. The crystals were filtered out, washed with 1-butanol, and dried in vacuo at room temperature.

The tetracoordinated complexes are rose colored, the hexacoordinated ones are white, and the $Fe(DMTU)_7(BF_4)_2$ is grayish white. The analytical results are in agreement with the proposed formulas and are found in Supplementary Table 1.

Synthesis of $Fe(DMTU)_5(BF_4)_2$. Stoichiometric amounts of $Fe(BF_4)_2 \cdot 6H_2O$ and DMTU, dissolved in the minimum volume of 1-butanol, were mixed at room temperature. The resulting dark green solution was allowed to stand at 5 °C until the appearance of an abundant precipitate, which was removed by filtration, washed with 1-butanol, and dried in vacuo. The crystals are light blue and needle shaped. The analytical results are found in Supplementary Table 1.

Physical Measurements. Solid electronic spectra of a Nujol mull on filter paper were recorded with a Carl-Zeiss DMR 22 spectrophotometer.

Magnetic susceptibilities at room temperature were measured by the Faraday method using a Cahn 7600-RTL balance.

The Mössbauer spectra for polycrystalline samples were obtained in a conventional spectrometer with constant acceleration. The source was 10-mCi ^{57}Co in a Pd matrix. The reported isomer shift values are relative to sodium nitroprusside. The data were adjusted with an iterative least-squares method.

Crystal and Intensity Data. Crystals of $Fe(DMTU)_6(BF_4) \cdot DMTU$ are monoclinic (space group $C2/c$, $Z = 4$) in a unit cell with the following dimensions: $a = 13.561$ (3), $b = 24.008$ (4), $c = 14.290$ (2) Å; $\beta = 91.36$ (2)°; $V = 4651$ (1) Å^3; d(calcd) = 1.37, d(exptl) = 1.38 g·cm^{-3}. A pale yellow crystal in the shape of a rectangular prism, 0.1 × 0.2 × 0.5 mm, was used to collect 5800 independent reflections, with 3037 having intensities above 3.0σ ($2.0 < 2\theta < 55.0°$). No absorption correction was made ($\mu = 7.06$ cm^{-1}). The diffractometer used was a Syntex $P2_1$ with Mo Kα radiation ($\lambda = 0.71869$ Å) and a graphite monochromator. The temperature of measurement was 295 K.

Structure Determination and Refinement.[5] The Fe atom, located by Patterson synthesis, was found to occupy an inversion center. The remaining atoms were found by difference Fourier synthesis. Refinement proceeded by using a full-matrix least-squares calculation. Anisotropic temperature factors for all the non-hydrogen atoms were added in the latter stages of refinement. Some hydrogen atoms were located, and the

Table I. Final Positional Parameters, with Estimated Standard Deviations in Parentheses, for $[Fe(SC(NHCH_3)_2)_6](BF_4)_2 \cdot SC(NHCH_3)_2$

atom	*X/a*	*Y/b*	*Z/c*
Fe	0.25	0.25	0.5
S1	0.31361 (8)	0.30500 (4)	0.64642 (7)
C1	0.3634 (3)	0.3695 (2)	0.6221 (3)
N11	0.3944 (3)	0.3811 (1)	0.5374 (3)
N12	0.3702 (3)	0.4078 (2)	0.6875 (3)
C11	0.4338 (5)	0.4347 (2)	0.5090 (4)
C12	0.3410 (6)	0.3995 (3)	0.7854 (4)
S2	0.29532 (9)	0.17046 (4)	0.60468 (8)
C2	0.3412 (3)	0.1134 (2)	0.5464 (4)
N21	0.3533 (4)	0.0653 (2)	0.5917 (3)
N22	0.6362 (3)	0.1163 (2)	0.4585 (3)
C21	0.3286 (8)	0.0569 (3)	0.6915 (5)
C22	0.4003 (5)	0.0699 (2)	0.4007 (4)
S3	0.41644 (8)	0.25539 (5)	0.41262 (7)
C3	0.5147 (3)	0.2326 (2)	0.4800 (3)
N31	0.5166 (3)	0.2395 (2)	0.5721 (3)
N32	0.5920 (3)	0.2070 (2)	0.4409 (3)
C31	0.5938 (5)	0.2183 (3)	0.6357 (4)
C32	0.5967 (5)	0.1942 (3)	0.3415 (4)
Sun[a]	0.0	0.02093 (7)	0.75
Cun[a]	0.0311 (7)	0.0889 (4)	0.7617 (9)
N1un[a]	0.102 (1)	0.1074 (7)	0.812 (1)
N2un[a]	−0.0159 (8)	0.1284 (4)	0.7142 (8)
C1un[a]	0.1434 (8)	0.1596 (5)	0.8233 (9)
C2un[a]	−0.124 (2)	0.112 (2)	0.662 (2)
B	0.7987 (7)	0.4250 (3)	0.4939 (6)
F1	0.7329 (4)	0.4607 (2)	0.4659 (6)
F2	0.8536 (3)	0.4446 (2)	0.5659 (4)
F3	0.8636 (6)	0.4199 (3)	0.4235 (5)
F4	0.7639 (3)	0.3739 (2)	0.5100 (3)

[a] Uncoordinated methylthiourea; disordered.

Table II. Bond Distances (Å), with Estimated Standard Deviations in Parentheses, for $[Fe(SC(NHCH_3)_2)_6](BF_4)_2 \cdot SC(NHCH_3)_2$

Fe–S1	2.604 (1)	C3–N31	1.327 (6)
Fe–S2	2.494 (1)	C3–N32	1.349 (6)
Fe–S3	2.608 (1)	N31–C31	1.462 (7)
S1–C1	1.729 (4)	N32–C32	1.460 (7)
C1–N11	1.319 (6)	Sun–Cun	1.70 (1)
C1–N12	1.314 (6)	Cun–Niun	1.25 (2)
N11–C11	1.458 (7)	Cun–N2un	1.32 (2)
N12–C12	1.474 (7)	N1un–C1un	1.41 (2)
S2–C2	1.727 (5)	N2un–C2un	1.69 (2)
C2–N21	1.329 (6)	B–F1	1.29 (1)
C2–N22	1.299 (6)	B–F2	1.34 (1)
N21–C21	1.497 (9)	B–F3	1.36 (1)
N22–C22	1.484 (7)	B–F4	1.334 (9)
S3–C3	1.713 (4)		

Table III. Bond Angles (deg), with Estimated Standard Deviations in Parentheses, for $[Fe(SC(NHCH_3)_2)_6](BF_4)_2 \cdot SC(NHCH_3)_2$

S1–Fe–S2	80.45 (8)	S3–C3–N31	121.0 (3)
S1–Fe–S3	94.92 (8)	S3–C3–N32	121.2 (3)
S2–Fe–S3	96.97 (8)	C3–N31–C31	124.8 (4)
Fe–S1–C1	114.6 (2)	C3–N32–C32	123.4 (4)
Fe–S2–C2	113.9 (2)	N31–C3–N32	117.9 (3)
Fe–S3–C3	112.7 (2)	Sun–Cun–N1un	124 (1)
S1–C1–N11	120.4 (3)	Sun–Cun–N2un	121 (1)
S1–C1–N12	120.3 (3)	Cun–N1un–C1un	131 (1)
C1–N11–C11	124.6 (3)	Cun–N2un–C2un	119 (1)
C1–N12–C12	124.3 (4)	N1un–Cun–N2un	114 (1)
N11–C1–N12	119.3 (3)	F1–B–F2	111.6 (6)
S2–C2–N21	120.0 (3)	F1–B–F3	106.2 (6)
S2–C2–N22	121.1 (3)	F1–B–F4	114.7 (6)
C2–N21–C21	123.6 (4)	F2–B–F3	104.3 (6)
C2–N22–C22	125.9 (5)	F3–B–F4	106.3 (6)
N21–C2–N22	118.9 (3)		

---

(11) Postgate, J. R., Ed. *The Chemistry and Biochemistry of Nitrogen Fixation*; Plenum: New York, 1971.

(12) Bray, R. C.; Swan, J. C. *Struct. Bonding* (*Berlin*) **1972,** *11*, 107.

(13) Albertsson, J.; Oskarsson, A.; Stahl, K.; Svensson, C.; Ymer, I. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1981**, *B37*, 50.

(14) Raston, C. L.; Sly, W. G.; White, A. H. *Aust. J. Chem.* **1980**, *33*, 221.

(15) Albertsson, J.; Oskarsson, A.; Nygren, M. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1979**, *B35*, 1473.

(16) Bereman, R. D.; Churchill, M. R.; Nalewajek, D. *Inorg. Chem.* **1979**, *18*, 3112.

(17) Chaps, G. E.; Mc Cann, S. W.; Wickman, H.; Sherwook, R. C. *J. Chem. Phys.* **1974**, *60*, 990.

(18) Healy, P. C.; White, A. H.; Hoskins, B. F. *J. Chem. Soc., Dalton Trans.* **1972**, 1369.

Table IV. Magnetic Moments,[a] Solid-State Electronic Spectra,[b] and Mössbauer Data for Thiourea Complexes of Iron(II)

			Mössbauer data				
						absorption: % (Γ^g)	
compd	μ_{eff}	spectra[c]	T^d	δ^e	$\Delta E_Q{}^f$	line 1[h]	line 2
$Fe(DMTU)_4(ClO_4)_2$	5.1	6.56	295	0.91	3.35	4.8 (0.28)	4.8 (0.29)
			100	0.94	3.41	9.2 (0.28)	9.5 (0.31)
$Fe(DMTU)_4(BF_4)_2$	5.1	6.56	295	0.92	3.28	4.2 (0.30)	4.4 (0.29)
			100	0.97	3.41	13.1 (0.29)	12.0 (0.32)
$Fe(DETU)_4(ClO_4)_2$	5.0	6.56	295	0.88	3.21	1.0 (0.30)	1.0 (0.29)
			100	0.89	3.45	2.8 (0.39)	2.8 (0.39)
$Fe(DETU)_4(BF_4)_2$	5.1	6.56	295	0.89	3.18	0.7 (0.30)	0.7 (0.29)
			100	0.92	3.35	1.7 (0.43)	1.3 (0.44)
$Fe(DMTU)_5(BF_4)_2$	5.1	8.70	295	1.06	3.13	4.4 (0.25)	4.1 (0.27)
			100	1.12	3.30	8.1 (0.28)	8.0 (0.28)
$Fe(DMTU)_6(ClO_4)_2$	5.3	9.8	295	1.20	3.23	3.7 (0.30)	3.8 (0.30)
			100	1.25	3.33	9.1 (0.32)	9.1 (0.32)
$Fe(DMTU)_7(BF_4)_2$	5.2	10.1	295	1.18	3.49	3.6 (0.27)	3.2 (0.28)
			100	1.21	3.50	8.6 (0.25)	8.2 (0.28)
$Fe(NETU)_6(ClO_4)_2$	5.1	10.3	295	1.18	3.36	5.6 (0.29)	5.9 (0.26)
			90	1.30	3.54	17.4 (0.31)	17.5 (0.31)
$Fe(NETU)_6(BF_4)_2$	5.1	10.2	295	1.24	3.18	6.0 (0.29)	5.8 (0.29)
			90	1.31	3.39	18.0 (0.31)	17.7 (0.31)
$Fe(DETU)_6(ClO_4)_2$	5.1	10.0	295	1.17	3.15	1.5 (0.42)	1.6 (0.39)
			100	1.22	3.51	6.5 (0.29)	5.5 (0.35)
$Fe(DETU)_6(BF_4)_2$	5.1	9.9	295	1.21	3.24	0.3 (0.42)	0.3 (0.42)
			100	1.22	3.51	5.6 (0.35)	5.1 (0.38)
$Fe(DPTU)_6(BF_4)_2{}^i$	5.0	10.3	90	1.31	3.47	11.1 (0.31)	10.1 (0.31)
$Fe(DPTU)_6(ClO_4)_2{}^i$	5.1	9.8	90	1.33	3.56	3.4 (0.47)	3.7 (0.45)

[a] μ_{eff}, in Bohr magnetons at room temperature. [b] Nujol mull, d–d-transition region in $cm^{-1} \times 10^3$. [c] For octahedral complexes, $^5T_{2g} \rightarrow {}^5E_g$ (medium broad bands); for tetrahedral complexes, $^5E \rightarrow {}^5T_2$ (strong broad bands); for pentacoordinated complex, see text. [d] Temperature in K. [e] Isomer shift relative to sodium nitroprussiate in mm/s. [f] Quadrupole splitting in mm/s. [g] Line width in mm/s. [h] Line 1 and line 2 are related to low and high speeds, respectively. [i] No absorption observed at room temperature.

others were placed at calculated positions. Hydrogen atoms were not refined. Standard statistical weighting was used, leading to a final R = 0.045 and R_w = 0.044. The final coordinates are listed in Table I. Bond distances and angles are given in Tables II and III. Anisotropic thermal parameters and least-square planes are given in Supplementary Tables 2 and 3. The structure factors are found in Supplementary Table 4.

Results and Discussion

The infrared spectra of all the complexes studied show that tetrafluoroborate and perchlorate are ionic in all cases[19] and that the thioureas are coordinated through the sulfur atom to the metal.[20] Magnetic susceptibilities and electronic d–d-transition data are summarized in Table IV. The assignments due to tetrahedral or octahedral high-spin structures are shown. Table IV also presents the Mössbauer data at 295 and 100 K for all the complexes studied. Typical Mössbauer spectra at these temperatures are shown in Figure 1. The δ parameters ($0.88 < \delta < 1.27$ mm/s at T = 295 K) and magnetic susceptibility data are consistent with a high-spin distribution for Fe(II) with sulfur ligands.[21] The ΔE_Q values greater than 3.0 mm/s in all cases agree with a singlet orbital ground state for a high-spin distorted octahedral or tetrahedral Fe(II) environment.[6] The complexes $Fe(DMTU)_n(BF_4)_2$ (n = 5, 7) will be discussed later.

The only reported[22,23] tetrahedral complexes of iron with thioureas, FeL_2X_2 (X = Cl, Br), have $10Dq$ values at ca. 5260 cm^{-1}. The tetrahedral complexes $(FeL_4)X_2$ synthesized in this work show $10Dq \sim 6560$ cm^{-1}.

Assuming linear averaging, with a value of $10Dq \sim 4050$ cm^{-1} for $FeCl_4{}^{2-}$, $10Dq$ becomes 6470 cm^{-1} for $Fe(DETU)_4{}^{2+}$. This is in reasonable agreement with the experimental results, confirming approximate tetrahedral symmetry for these complexes.

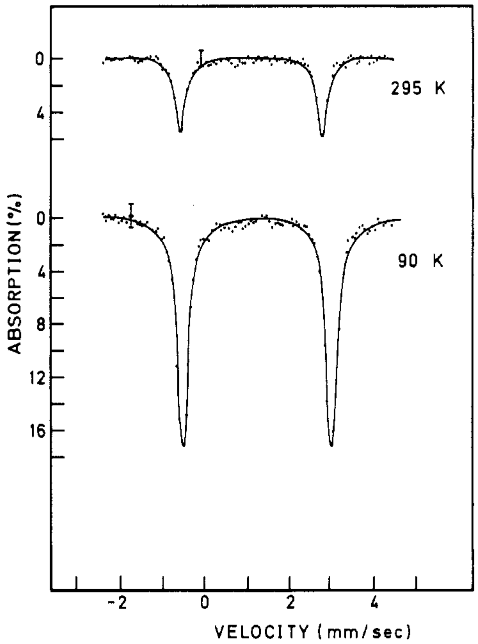

Figure 1. Mössbauer spectra for $[Fe(NETU)_6](ClO_4)_2$ at two temperatures. Isomer shift is referenced to $Na_2Fe(CN)_5NO{\cdot}2H_2O$ (I: error bar).

Table V. Crystal Field Distortions, Δ_T, in Tetrahedral Iron(II) Complexes of Thiourea Estimated from the Mössbauer Parameters

complex	Δ_T, cm^{-1}	complex	Δ_T, cm^{-1}
$Fe(DMTU)_4(BF_4)_2$	819	$Fe(DETU)_4(BF_4)_2$	721
$Fe(DMTU)_4(ClO_4)_2$	963	$Fe(DETU)_4(ClO_4)_2$	686

However, due to distortion of the tetrahedra, the d_{z^2} and $d_{x^2-y^2}$ orbitals are not degenerate. The energy difference between these resulting states, Δ_T, is calculated according to Ingalls:[24]

$$\Delta_T = kT \ln \frac{\Delta E_Q(0) + \Delta E_Q}{\Delta E_Q(0) - \Delta E_Q}$$

---

(19) (a) Hathaway, B. J.; Holah, D. G.; Hudson, M. *J. Chem. Soc.* **1963**, 4586. (b) Marcotrigiano, G. O.; Peryonal, G.; Battistuzzi, R. *Inorg. Chim. Acta* **1974**, *9*, 5.

(20) (a) Dwarkanath, K.; Sathyanarayana, D. N. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 2084. (b) Ritchie, R. K.; Spedding, H.; Steele, D. *Spectrochim. Acta, Part A* **1971**, *27A*, 1597.

(21) Reiff, W. M. In *Mössbauer Effect Methodology*; Gruvermann, I. J., Seidel, C. W., Eds.; Plenum: New York, 1973; Vol. 8, p 79.

(22) Russo, U.; Calogero, S.; Burrierci, N.; Petrera, M. *J. Inorg. Nucl. Chem.* **1979**, *41*, 25.

(23) Birchal, T.; Morris, M. F. *Can. J. Chem.* **1972**, *50*, 211.

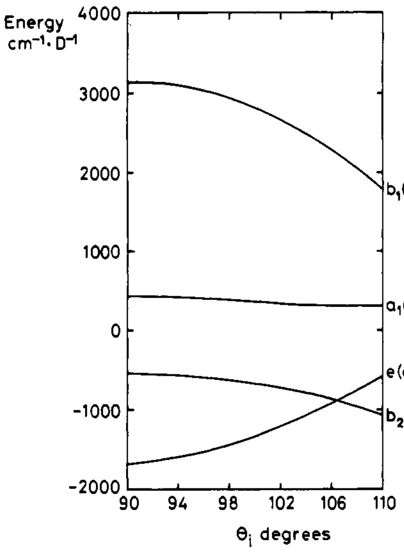

Figure 2. Energy level diagram for iron(II) 3d orbital (or terms) in a square-pyramidal crystal field and its apical (θ_i) dependence.

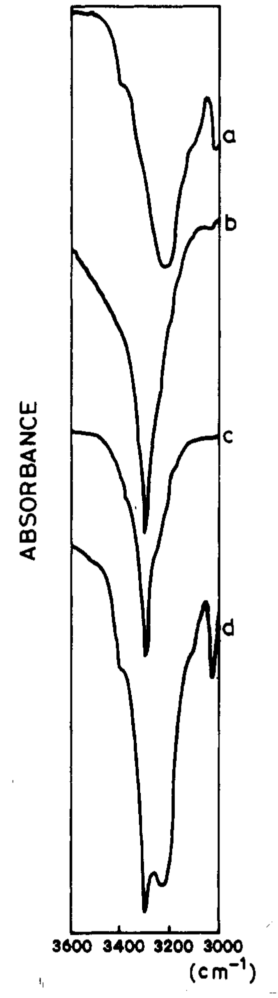

Figure 3. Infrared spectra (solid Nujol mull, N–H stretching region): (a) DMTU; (b) $[Fe(DMTU)_4](BF_4)_2$; (c) $[Fe(DMTU)_5](BF_4)_2$; (d) $Fe(DMTU)_7(BF_4)_2$.

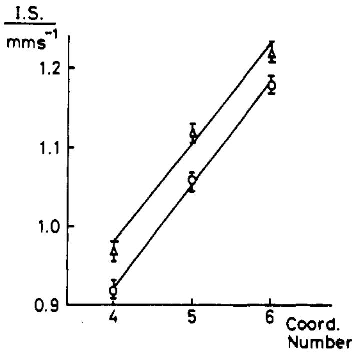

Figure 4. Isomer shift, δ, vs. coordination number in $Fe(DMTU)_n(BF_4)_2$ (n = 4, 5, 7): ○, room temperature; △, 100 K (I: error bar).

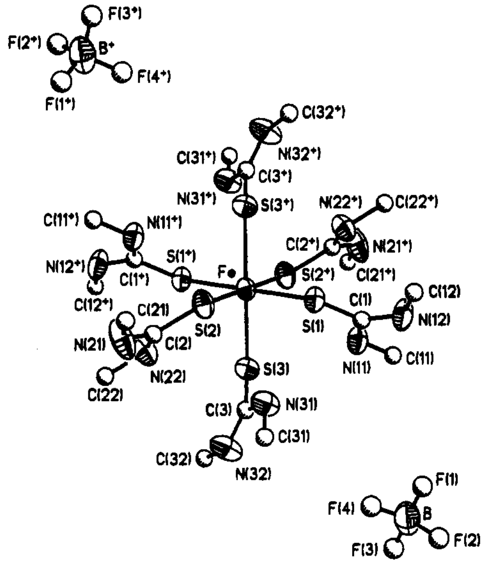

Figure 5. SHELXTL drawing of $[Fe(SC(NHCH_3)_2)_6]^{2+}$ with thermal ellipsoids shown at the 50% probability level. Hydrogen atoms are omitted for clarity. Iron is located at an inversion center. Symmetry-related atoms are labeled by +.

where $\Delta E_Q(0)$ and ΔE_Q are the quadrupole splitting values for 0 and T K of temperature, respectively. $\Delta E_Q(0)$ was obtained by extrapolation. Δ_T values are shown in Table V. The values obtained are in agreement with those reported previously for FeL_2X_2 complexes (L = thiourea, *N*-methylthiourea, DMTU; X = Cl, Br).[22,23] The large distortion observed therein has been interpreted in terms of the steric nature of the ligands and differences in the covalence of the FeX and FeL bonds. We find here the Δ_T values are 10–15% of $10Dq$ and show rather clearly that the distortion from T_d symmetry may be due mainly to steric effects produced by the substituents of the thiourea. There is no observable effect due to the perchlorate or tetrafluoroborate anions. The ΔE_Q values found for complexes with the same ligand did not show any significant differences that can be correlated with the nature of the anions.

For hexacoordinated complexes, the electronic spectra show transitions typical (Table IV) of octahedral symmetries. The ΔE_Q is greater than 3.0 mm/s (Table IV) and agrees with values found in similar complexes.[8] Thus, the ΔE_Q of the hexacoordinated complexes may be interpreted in terms of an orbital singlet ground state,[6,7] due to distortions of the local crystal field from octahedral symmetry.

It is possible to compare δ values for tetrahedral and octahedral complexes with the same ligand. The observed values are the expected ones; i.e., δ is lower when the coordination number diminishes from 6 to 4.[25] For example, at room temperature the octahedral complex $Fe(DETU)_6(BF_4)_2$ has a δ value of 1.21 mm/s while the tetrahedral $Fe(DETU)_4(BF_4)_2$ has a value of 0.89 mm/s. These observations confirm the assumption that when the coordination number diminishes, the "s" electronic density at the iron nucleus is increased. Another effect that also may contribute to an increase of this density might be the electronic back-donation

---

(24) Ingalls, R. *Phys. Rev.* [*Sect.*] *A* **1964**, *133*, 787.

(25) Greenwood, N. N.; Gibb, T. C. *Mössbauer Spectroscopy*; Chapman and Hall: London, 1971; p 59.

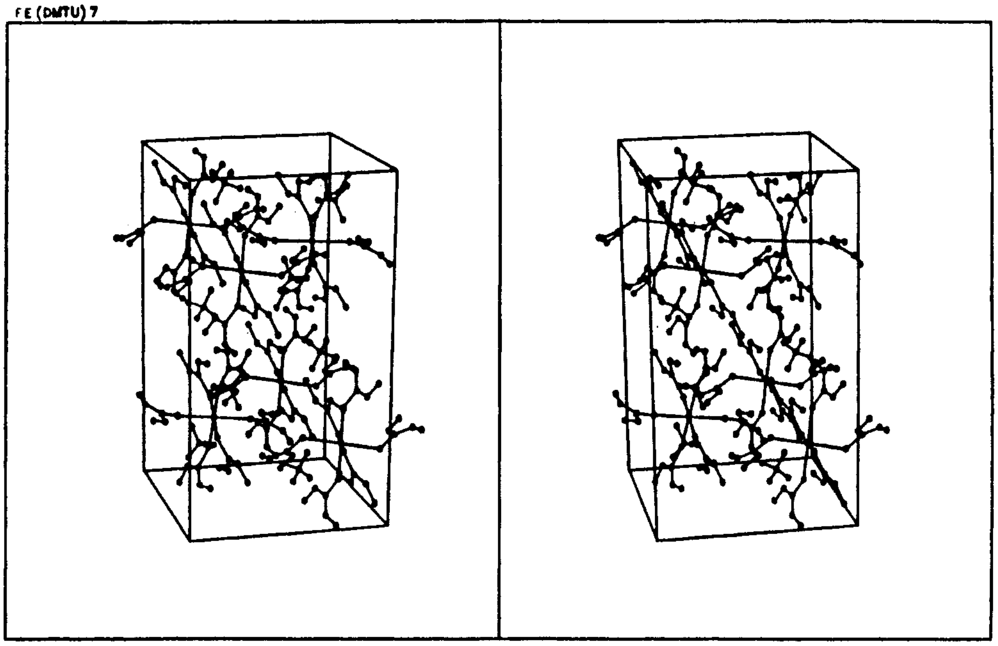

Figure 6. SHELXTL drawing of the unit cell for $[Fe(SC(NHCH_3)_2)_6](BF_4)_2{\cdot}SC(NHCH_3)_2$.

from the metal 3d to the ligand π^* orbitals.[26] This is the first case in which it has been possible to study Mössbauer parameters for high-spin Fe(II) in octahedral and tetrahedral symmetries with the same monodentate soft sulfur ligand.

The existence of a complex with the formula $Fe(DMTU)_5(BF)_4$ might be explained by the electronic spectrum, which shows one medium-intensity d–d transition at 8700 cm^{-1}. This value together with the δ value, intermediate between those for tetra- and hexacoordination (Table IV), suggests a pentacoordinated complex.[27] The pentacoordination could be related to two regular symmetries: trigonal bipyramidal and square-base pyramidal (BP and SP, respectively, hereafter). In both cases the orbital ground state is a doublet, so $\Delta E_Q < 2.0$ mm/s at low temperatures is expected. For a distorted BP structure ($D_{3h} \rightarrow C_{3v}$), e_1 is still the lowest energy level, so the ΔE_Q value remains unchanged.

A distortion occurs in a SP complex when the metal atom is above the plane, but the C_{4v} symmetry does not change. The relative values of the 3d orbitals change, however, with the distortion. They were calculated by using a simple crystal field model.[28] When the position of the metal changes, the apical angle, θ, varies. In Figure 2 the effect produced on the 3d orbitals is shown for $90 \leq \theta \leq 110°$. For an angle >106.8°, the ground state is b_2 (d_{xy}). This means that ΔE_Q will be greater than 2.0 mm/s at low temperatures. These results suggest that in this complex the iron has a distorted SP environment (Table IV). Similar results have been found for iron(II) with macrocyclic ligands[29] and for pentacoordinated complexes of cobalt(II) and nickel(II);[30] also, theoretical estimates exist.[31] From Figure 2 it is possible to assign the electronic band observed at 8700 cm^{-1} to a $^5B_2 \rightarrow {}^5B_1$ transition. Similar results for SP symmetries have been found.[32] Transitions to ^5E and $^5A_1$ should appear in the infrared spectra.

The IR spectrum of $Fe(DMTU)_7(BF_4)_2$ shows that one of the DMTU molecules is not coordinated to the iron directly (Figure 3). In addition, the electronic spectrum shows a band at 10.1 $\times$ 10^3 cm^{-1} typical of octahedral complexes. From Figure 4 it is possible to correlate the isomer shift with the coordination numbers for the complexes $Fe(DMTU)_n(BF_4)_2$ and to assign $n = 6$ for the complex under discussion. So, the proposed structure would be $Fe(DMTU)_6(BF_4)_2{\cdot}DMTU$. This is confirmed by the X-ray diffraction results.

From Tables II–IV and the drawing of the molecule shown in Figure 5, it is found that the iron geometry is a distorted, tetragonally compressed octahedron. The dimethylthiourea ligands are planar (root-mean-square deviations average 0.026 Å) for S, C, and N atoms. The uncoordinated dimethylthiourea occupies a twofold axis and is disordered, and the tetrafluoroborate anions also show a distortion of the regular tetrahedra. Figure 6 is a SHELXTL drawing of the unit cell, which shows the glide plane of the space group quite clearly.

Substantial work has been published in the past[1-5,10-18] on various iron–sulfur systems. These studies generally have been of Fe(III) with ionic dithiolate or thioxanthate ligands, resulting in low-spin complexes distorted by the ligand "bite". There have been relatively few studies[33,34] of Fe(II) with neutral, soft sulfur-bonded ligands, such as thiourea. Indeed, this is the first report of high-spin Fe(II) coordinatively saturated with sulfur ligands.

The ground term of high-spin Fe(II) is $^5T_{2g}$. Jahn–Teller distortion should be present, but with a T ground term, it is expected to be small. Thus, the magnitude of the distortion found in this complex is surprising: it is larger than has been found for many E-term complexes.[35] Not only are the bond angles substantially distorted from octahedral geometry, but there is sizable tetragonal compression as well. The equatorial Fe–S bonds are typical of those found in other high-spin Fe(II)–S systems,[33,34] but the axial bonds are fully 0.12 Å shorter.

The ground term for a tetragonal compression is expected to be an orbital singlet, $^5B_{2g}$. The Mössbauer results are consistent with this fact because the quadrupole splitting found at room temperature, 3.48 mm/s, is in the expected range[6,36] for this kind of distortion.

The planarity of the thiourea ligands indicates that they contain a delocalized π system. The angles at each sp^2-hybridized carbon

---

(26) Vertês, A.; Korecz, L.; Burger, K. *Mössbauer Spectroscopy*; Elsevier: Amsterdam, 1979; Chapter 2.

(27) Edwards, P. R.; Johnson, C. E.; Williams, R. S. P. *J. Chem. Phys.* **1967**, *47*, 2074.

(28) Lever, A. B. P. *Inorganic Electronic Spectroscopy*; Elsevier: Amsterdam, 1968; Chapter 4.

(29) Reiff, W. M. *Inorg. Chem.* **1974**, *13*, 239.

(30) (a) Preer, J. R.; Gray, H. B. *J. Am. Chem. Soc.* **1970**, *92*, 7306. (b) Caride, A. O.; Panepucci, H.; Zanette, S. I. *J. Chem. Phys.* **1971**, *55*, 3651.

(31) Morassi, R.; Bertini, I.; Sacconi, L. *Coord. Chem. Rev.* **1973**, *11*, 343.

(32) Karayannis, N. M.; Bradshaw, E. E.; Pytlewski, L. L.; Labec, M. M. *J. Inorg. Nucl. Chem.* **1970**, *32*, 1079.

(33) Valle, M.; Russo, U.; Calogero, S. *Transition Met. Chem.* (*Weinheim, Ger.*) **1980**, *5*, 26.

(34) Russo, U.; Graziani, R.; Calogero, S.; Casellato, U. *Transition Met. Chem.* (*Weinheim, Ger.*) **1979**, *4*, 82.

(35) Fackler, J. P.; Avdeef, A.; Costamagna, J. A. *Inorg. Chem.* **1974**, *13*, 1864.

(36) Vertês, A.; Korecz, L.; Burger, K. *Mössbauer Spectroscopy*; Elsevier: Amsterdam, 1979; p 70.

and nitrogen atom are very nearly 120° (Table III). The nitrogens and the sulfur each donate an electron pair to the π molecular orbital, making a six-electron system. The large Jahn–Teller splitting may be explained by assuming donation of electron density from this π system to the antibonding orbitals on the iron atom. Since the d_{xy} orbital contains the odd electron, this would be antibonding toward the equatorial ligands. Thus, this "tetragonal compression" is actually an "equatorial expansion".

It is observed that the orientation of the methyl substituents is cis–trans relative to sulfur, which confirms the low-temperature ^{1}H NMR results found previously[37,38] and rules out the possible trans–trans configuration in these cases.

The distortion observed in the tetrafluoroborate groups is of the same magnitude as that found previously by Figgis et al. for perchlorate in the complex $[Ti(urea)_6](ClO_4)_3$.[39,40] In that case, a hydrogen bond type interaction between urea and perchlorate produced a distortion of the octahedra. By analogy, the results observed by Mössbauer spectroscopy at different temperatures for iron(II) perchlorate complexes with substituted thioureas, $[Fe(dicyclohexylthiourea)_6](ClO_4)_2$[6] and $[Fe(dibutylthiourea)_6](ClO_4)_2$[9] among others, show a notable distortion of the "FeS_6" environment interpreted in terms of a probable thiourea–perchlorate interaction via hydrogen bridges.

The results found in this structure show an unusual "FeS_6" distortion. From the variation of the quadrupole splitting with temperature as has been done for tetrahedral complexes[24] (vide supra), it is possible to calculate an energy difference between the resulting states b_{2g} (d_{xy}) and e_g (d_{xz}, d_{yz}) of ca. 1400 cm^{-1}. This value is higher than those observed for the tetragonally compressed complexes $[Fe(thiourea)_4Cl_2]$ and $[Fe(thiourea)_4I_2]$, which have Δ_T values of 860 and 750 cm^{-1}, respectively.[22] It is believed that the tetrafluoroborates and the free thiourea in the packing of the crystal help to induce the observed distortions.

The three following factors must be taken into account in order to study the effect of the substituent on the thiourea and the nature of the anion on the properties and structures of the complexes. (a) Electronic: different substituents induce a change in the electronic density of the sulfur donor atom, which affects the σ-donor and π-acceptor capacity of the ligand. (b) Steric: the volume occupied by the substituent governs the number of thioureas present around the iron. (c) Solid state: hydrogen bonding between tetrafluoroborate and the substituted thioureas can be important. It is not obvious what causes the different stereochemistries and subsequent Mössbauer data for the different substituted thioureas. Certainly, the crystal field stabilization energy, steric effects, and anion binding play important roles.

However, it is possible to determine the importance of the specific anion in the final structure present for a complex. This case is clearly shown in Table IV for DMTU as a ligand. The existence of tetrahedral and octahedral species is found only with $Fe(ClO_4)_2$ while with $Fe(BF_4)_2$ three different species, namely with 4 (tetrahedral), 5, and 7 ligands, were obtained. These structural differences may be explained as due to different interactions (via hydrogen bonding, for example) of tetrafluoroborate and perchlorate in the solid phase. In addition, some distinct order–disorder phenomena in the anions[41] are possible.

Finally, the observed Mössbauer absorption for the complexes increases when the temperature is lowered, but for DPTU complexes no absorption is observed at room temperature. The values of the absorption are apparently dependent on the nature of the ligand, the effect of the anion being less important. So, for the DMTU tetrahedral complexes an absorption value of 4.4–4.8% is observed, while for tetrahedral DETU complexes it is 0.7–1.0% at room temperature. For the octahedral complexes values of 3.6–3.7% for DMTU and 1.5–0.3% for DETU are observed. The observed line widths at different temperatures show an irregular behavior, and some of them increase when the temperature is lower, as is observed for tetrahedral DETU complexes. "Since line broadening may be carried by many factors acting simultaneously, interpretation of the nature for a general case is a very complicated problem."[42] A further discussion on the nature of the line broadening will be published elsewhere.

Acknowledgment. Part of this work was supported by Grant No. Q549-8344 of Servicio de Desarrollo Científico, Universidad de Chile, and Dirección de Investigaciones Científicas y Tecnológicas, Universidad de Santiago. The National Science Foundation (Grant CHE 8408414) supported the crystallographic study, and The Welch Foundation also contributed to the effort at Texas A&M. J.G. thanks the Consejo Nacional de Investigación Científica y Tecnológica (CONICYT) Santiago, Chile, for a fellowship.

Registry No. $Fe(DMTU)_4(ClO_4)_2$, 82704-42-5; $Fe(DMTU)_4(BF_4)_2$, 82704-43-6; $Fe(DETU)_4(ClO_4)_2$, 82704-45-8; $Fe(DETU)_4(BF_4)_2$, 82704-46-9; $Fe(DMTU)_5(BF_4)_2$, 82541-82-0; $Fe(DMTU)_6(ClO_4)_2$, 60459-64-5; $Fe(DMTU)_6(BF_4)_2{\cdot}(DMTU)$, 82704-60-7; $Fe(NETU)_6(ClO_4)_2$, 82704-51-6; $Fe(NETU)_6(BF_4)_2$, 82704-50-5; $Fe(DETU)_6(ClO_4)_2$, 82704-53-8; $Fe(DETU)_6(BF_4)_2$, 82704-54-9; $Fe(DPTU)_6(BF_4)_2$, 82704-56-1; $Fe(DPTU)_6(ClO_4)_2$, 82704-57-2.

Supplementary Material Available: Tables 1–3, giving analytical data, anisotropic thermal parameters, and least-squares planes (3 pages); Table 4, listing observed and calculated structure factors (18 pages). Ordering information is given on any current masthead page.

---

(37) Granifo, J.; Costamagna, J.; Garrao, A.; Pieber, M. *J. Inorg. Nucl. Chem.* **1980**, *42*, 1587.

(38) Walter, W.; Ruess, K. P. *Justus Liebigs Ann. Chem.* **1971**, *746*, 541.

(39) Figgis, B. M.; Wadley, L. G. B.; Graham, J. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1972**, *B28*, 187.

(40) Figgis, B. N.; Wadley, L. G. B. *Aust. J. Chem.* **1972**, *25*, 2233.

(41) Figgis, B. N.; Wadley, L. G. B.; Gerloch, M. *J. Chem. Soc., Dalton Trans.* **1973**, 238.

(42) Goldanskii, V. I.; Marakov, E. F. In *Chemical Applications of Mössbauer Spectroscopy*; Goldanskii, B. I., Herber, R. H., Eds.; Academic: New York, 1968; p 102.