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Transition Metal Complexes with Thiosemicarbazide-Based Ligands. 14.[1] Iron(IV) Complexes with 2,4-Pentanedione Bis(*S*-alkylisothiosemicarbazone). Crystal and Molecular Structure of Iodo{2,4-pentanedione bis(*S*-ethylisothiosemicarbazonato)(3–)}iron(IV)

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A method of template synthesis yielded the following complexes of iron(IV) and 2,4-pentanedione bis(*S*-alkylisothiosemicarbazone) (H_3R_2L): [Fe(R_2L)I], R = CH_3 (**1**), C_2H_5 (**2**), *n*-C_3H_7 (**3**), and *n*-C_4H_9 (**4**). The X-ray analysis of **2** showed the crystal belongs to the triclinic system, space group $P\bar{1}$, with $a = 8.622$ (1) Å, $b = 8.764$ (1) Å, $c = 13.058$ (1) Å, $\alpha = 73.38$ (1)°, $\beta = 85.87$ (1)°, $\gamma = 68.96$ (1)°, $d_{calc} = 1.805$ g cm^{-3}, $Z = 2$, and molecular formula $C_{11}H_{19}FeIN_6S_2$. The structure was solved by direct method using SHELXS-86 and refined anisotropically by the least-squares method, employing 2137 unique reflections with $I \geq 3\sigma(I)$. The hydrogen atoms were located and refined by isotropic approximation. The final *R* was 0.022. Compound **2** has a square-pyramidal structure with the quadridentate ligand $(R_2L)^{3-}$ in the plane of the central ion (deviation from the pyramid base plane 0.389 Å) and I^- in the apical position. The results from magnetic measurements and Mössbauer spectra for **1**–**4** indicate the $S = 1$ state for the central ion. The complexes were also characterized by mass spectrometry.

Introduction

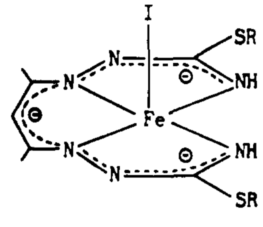
In stabilization of the unusually high oxidation states of transition metals, the electron-donor properties of the atoms and groups of the ligand and their tendency to form π-bonds play a substantial role. It has been known that the Fe(IV) oxidation state is stabilized by dithiocarbamates,[3-6] *o*-phenylenebis(dimethylarsine),[7-9] and 1,1-dicarbethoxy-2,2-ethylenedithiol.[10]

The interest in the problem of preparation of Fe(IV) compounds can be explained not only by their scarcity but also by the presence of Fe(IV) centers in the oxidized forms of some peroxidases.[11-13] Therefore, the knowledge of physicochemical properties of the model compounds of Fe(IV) is especially important for understanding the mechanism of functioning of these enzymes. Hence, the search for new types of ligands for the synthesis of these coordination compounds is justified.

Recently, a number of model porphyrin complexes containing Fe(IV) have been prepared.[14-17]

The ligands based on the *S*-alkylated isothiosemicarbazides $H_2NNC(SR)NH_2$ form with transition metals various coordination compounds.[18,19] Recent investigations showed that these ligands are also capable of stabilizing untypical oxidation states of 3d metals. Thus, the manganese(IV) complexes and mixed-valence tetranuclear complexes of iron(III,IV) with the *S*-alkylisothiosemicarbazide Schiff bases of *o*-oxybenzaldehydes have been recently prepared.[20,21]

In this work we present data on the synthesis, structure, and physicochemical properties of the coordination compounds of iron(IV) with 2,4-pentanedione bis(*S*-alkylisothiosemicarbazones) (H_3R_2L) of the general formula [Fe(R_2L)I]:



R = CH_3 (1), C_2H_5 (2),
n-C_3H_7 (3), *n*-C_4H_9 (4)

[Fe(R_2L)I]

Experimental Section

All chemicals used were analytical reagent grade. *S*-Alkylisothiosemicarbazide hydriodide and sodium acetylacetonate monohydrate were prepared according to known procedures, described in refs 22 and 23

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respectively. Iron was determined by the gravimetric method as Fe_2O_3, whereas the C, H, and N contents were determined by standard micromethods.

The electron impact mass spectra were measured on a MX-1320 double-focusing mass spectrometer (PO "Nauchpribor", g. Orel, USSR) using the direct inlet system at 110–180 °C, a temperature of the ionization chamber 60–70 °C higher than the evaporation temperature, an emission current of 10 μA, and an ionization energy of 70 eV.

Magnetic susceptibilities were measured on a Gouy apparatus. Effective magnetic moments were calculated from the relation $\mu_{eff} = 2.828(\chi_M T)^{1/2}$, taking into account the diamagnetic corrections.[24]

^{57}Fe Mössbauer measurements were carried out with powder samples of about 100 mg in polyethylene containers of 19-mm diameter at 300, 195, and 80 K; spectra were recorded with a spectrometer consisting of a constant-acceleration electronic drive and an ICA-70 nuclear multichannel analyzer operating in the multiscaling mode. The γ-source used consisted of 15 mCi of ^{57}Co in chromium at room temperature, the calibration being effected with an iron-foil absorber. All velocity scales and isomer shifts are referenced to the sodium nitroprusside standard at 300 K. For conversion to the iron scale, –0.257 mm s^{-1} has to be added.

Synthesis of 1–4. The corresponding *S*-alkylisothiosemicarbazide hydriodide (10 mmol) was dissolved in 10 cm^3 of ethanol by heating. To this hot solution were added 0.70 g (5 mmol) of sodium acetylacetonate monohydrate in 8 cm^3 of ethanol, 2.00 g (5 mmol) of $Fe(NO_3)_3{\cdot}9H_2O$ in 10 cm^3 of ethanol, and finally 0.80 cm^3 of pyridine. After cooling, the crystals were separated by filtration and washed with ethanol and water, again with ethanol, and finally with ether. The yields were 0.80 g (35.5%), 0.80 g (33.5%), 0.71 g (28.1%), and 1.21 g (45.5%) for **1–4**, respectively.

The black-brown monocrystals of **2** were obtained from a saturated chloroform–ethanolic solution on prolonged thermostating of the solution at room temperature.

Complex Characterization. Iodo{2,4-pentanedione bis(*S*-methylisothiosemicarbazonato)(3–)}iron(IV), [Fe(Me$_2$L)I] (1). Anal. Calcd for $C_9H_{15}FeIN_6S_2$ (fw, 454.12): C, 23.80; H, 3.33; Fe, 12.30; N, 18.51. Found: C, 23.60; H, 3.46; Fe, 12.41; N, 18.53. μ_{eff}: 3.00 μ_B (292 K). MS: *m/z* 454 (M$^+$).

Iodo{2,4-pentanedione bis(*S*-ethylisothiosemicarbazonato)(3–)}iron(IV), [Fe(Et$_2$L)I] (2). Anal. Calcd for $C_{11}H_{19}FeIN_6S_2$ (fw, 482.17): C, 27.40; H, 3.97; Fe, 11.58; N, 17.43. Found: C, 27.11; H, 4.27; Fe, 11.72; N, 17.44. μ_{eff}: 2.99 μ_B (294 K). MS: *m/z* 482 (M$^+$).

Iodo{2,4-pentanedione bis(*S*-propylisothiosemicarbazonato)(3–)}iron(IV), [Fe(*n*-Pr$_2$L)I] (3). Anal. Calcd for $C_{13}H_{23}FeIN_6S_2$ (fw, 510.22): C, 30.60; H, 4.54; Fe, 10.95; N, 16.17. Found: C, 30.19; H, 4.64; Fe, 10.69; N, 17.03. μ_{eff}: 2.94 μ_B (294 K). MS: *m/z* 510 (M$^+$).

Iodo{2,4-pentanedione bis(*S*-butylisothiosemicarbazonato)(3–)}iron(IV), [Fe(*n*-Bu$_2$L)I] (4). Anal. Calcd for $C_{15}H_{27}FeIN_6S_2$ (fw, 538.28): C, 33.47; H, 5.06; Fe, 10.37; N, 15.61. Found: C, 33.07; H, 4.72; Fe, 10.06; N, 15.56. μ_{eff}: 2.96 μ_B (294 K), 2.90 μ_B (116 K). MS: *m/z* 538 (M$^+$).

Collection and Reduction of X-ray Data for Complex 2. The suitable black-brown platelike crystal of [Fe(Et$_2$L)I] (**2**), dimensions 0.22 × 0.20 × 0.11 mm, was mounted on an Enraf-Nonius CAD-4 diffractometer to collect reflection data. Elementary cell parameters were measured and refined from the results of 15 strong high-angle reflections of the *h*00, 0*k*0, and 00*l* type. The intensities were measured at 293 K using the ω–2ϕ scanning technique. The method of profile analysis of peaks for the monochromated Mo Kα radiation (λ = 0.710 69 Å) was employed. Three standard reflections were measured after collecting 100 reflections. Corrections were applied for Lorentz and polarization factors. An empirical absorption was applied taking into account the form of the crystal according to SHELXTL.[25] To determine and refine the crystal structure, 2137 reflections satisfying $I \geq 3\sigma(I)$ were used; the dependent reflections were averaged. The structure was solved by the direct method using the SHELXS-86 program[26] and atomic factors from ref 27, including anomalous dispersion (f, f' and f''). No extinction correction was made. The structure was refined by the full-matrix least-squares method with anisotropic approximations for C, N, S, Fe, and I and isotropic values for H. The H atoms were obtained from a differential Fourier synthesis. The refinement was carried out using the weighting scheme $w = 1/|\sigma(F) + 0.002496F^2|$. The crystallographic data, atom coordinates and temperature factors, interatomic distances, and angles are presented in Tables I–IV, respectively.

Table I. Crystallographic Data for Complex **2**

chem formula	$C_{11}H_{19}FeIN_6S_2$	fw	482.17
a, Å	8.622 (1)	space group	$P\bar{1}$ (No. 2)
b, Å	8.764 (1)	*T*, °C	20
c, Å	13.058 (1)	λ, Å	0.710 69
α, deg	73.30 (1)	ρ_{calcd}, g cm^{-3}	1.805
β, deg	85.87 (1)	μ, cm^{-1}	28.17
γ, deg	68.91 (1)	no. of measd reflcns	2564
hkl limits	$-8 \leqslant h \leqslant 8$		
	$-9 \leqslant k \leqslant 9$	no. of reflcns used in refinement	2137
	$0 \leqslant l \leqslant 13$		
2θ range, deg	$3 < 2\theta < 45$		
transm factors: max, min	0.786, 0.574	$R(F_o)$[a]	0.022
		$R_w(F_o)$[b]	0.026

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = |\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2|^{1/2}$; $w^{-1} = |\sigma(F) + 0.002496F^2|$.

Table II. Atom Coordinates and Equivalent Isotropic Temperature Factors (Å^2) with Their Esd's for Complex **2**

atom	*x*	*y*	*z*	U_{eq}[a] or *U*
I	0.36282 (2)	0.65019 (3)	0.69644 (2)	0.048 (1)
Fe	0.22117 (5)	0.49234 (5)	0.61843 (3)	0.033 (1)
S(1)	0.4831 (1)	–0.0249 (1)	0.81835 (7)	0.048 (1)
S(2)	0.2116 (1)	0.7911 (1)	0.28564 (6)	0.045 (1)
N(1)	0.3724 (4)	0.2664 (3)	0.6615 (2)	0.040 (1)
N(2)	0.2024 (3)	0.2413 (3)	0.8022 (2)	0.039 (1)
N(3)	0.1141 (3)	0.4000 (3)	0.7399 (2)	0.035 (1)
N(4)	0.0197 (3)	0.6709 (3)	0.5575 (2)	0.036 (1)
N(5)	0.0237 (3)	0.7637 (3)	0.4547 (2)	0.039 (1)
N(6)	0.2775 (3)	0.5445 (3)	0.4727 (2)	0.040 (1)
C(1)	0.3406 (4)	0.1785 (4)	0.7562 (2)	0.037 (1)
C(2)	–0.0314 (4)	0.4845 (4)	0.7770 (2)	0.038 (1)
C(3)	–0.1392 (4)	0.6383 (4)	0.7136 (2)	0.040 (1)
C(4)	–0.1208 (4)	0.7270 (4)	0.6086 (3)	0.037 (1)
C(5)	0.1662 (4)	0.6905 (4)	0.4151 (2)	0.040 (1)
C(6)	0.0315 (5)	0.9866 (5)	0.2530 (3)	0.047 (1)
C(7)	0.0470 (6)	1.0921 (6)	0.1406 (3)	0.059 (2)
C(8)	–0.2586 (5)	0.8836 (5)	0.5517 (3)	0.049 (2)
C(9)	–0.0768 (5)	0.4102 (5)	0.8878 (3)	0.052 (2)
C(10)	0.3789 (5)	–0.0967 (5)	0.9371 (3)	0.054 (1)
C(11)	0.4905 (7)	–0.2694 (6)	1.0023 (4)	0.070 (2)
H(1n)	0.440 (5)	0.231 (5)	0.638 (3)	0.01 (1)
H(6n)	0.402 (7)	0.475 (8)	0.445 (4)	0.09 (2)
H(3)	–0.257 (5)	0.693 (5)	0.739 (3)	0.06 (1)
H(61)	0.042 (7)	1.027 (9)	0.326 (5)	0.14 (2)
H(62)	–0.050 (5)	0.955 (5)	0.250 (3)	0.05 (1)
H(71)	0.074 (7)	1.032 (9)	0.077 (6)	0.11 (2)
H(72)	–0.062 (6)	1.202 (6)	0.133 (3)	0.07 (1)
H(73)	0.161 (7)	1.122 (7)	0.153 (4)	0.11 (2)
H(81)	–0.340 (5)	0.909 (4)	0.588 (3)	0.04 (1)
H(82)	–0.283 (9)	0.875 (10)	0.485 (7)	0.13 (2)
H(83)	–0.238 (4)	0.970 (5)	0.535 (3)	0.04 (1)
H(91)	–0.054 (6)	0.282 (8)	0.926 (4)	0.10 (2)
H(92)	–0.162 (6)	0.480 (6)	0.899 (4)	0.06 (1)
H(93)	0.014 (6)	0.397 (5)	0.936 (4)	0.07 (1)
H(101)	0.367 (6)	–0.013 (7)	1.003 (4)	0.09 (2)
H(102)	0.264 (5)	–0.105 (5)	0.911 (3)	0.06 (1)
H(111)	0.523 (5)	–0.344 (6)	0.969 (3)	0.07 (1)
H(112)	0.421 (6)	–0.311 (6)	1.073 (4)	0.08 (1)
H(113)	0.612 (8)	–0.269 (8)	1.014 (5)	0.12 (2)

[a] Equivalent isotropic U_{eq} for non-H atoms defined as one-third of the trace of the orthogonalized U(*i,j*) tensor; $U_{eq} = {}^1/_3 \times$ trace $\tilde{U}$.[27]

Results and Discussion

Complexes **1–4** were obtained by template reaction of the corresponding *S*-alkylisothiosemicarbazide hydriodide with sodium

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Table III. Bond Lengths (Å) for Complex **2**

Fe–I	2.578 (1)		
Fe–N(1)	1.884 (2)	Fe–N(6)	1.895 (3)
Fe–N(3)	1.900 (2)	Fe–N(4)	1.905 (2)
N(1)–C(1)	1.324 (4)	N(6)–C(5)	1.339 (3)
C(1)–N(2)	1.311 (4)	C(5)–N(5)	1.313 (4)
N(2)–N(3)	1.368 (3)	N(5)–N(4)	1.361 (3)
N(3)–C(2)	1.345 (4)	N(4)–C(4)	1.341 (4)
C(2)–C(3)	1.391 (3)	C(4)–C(3)	1.398 (4)
C(2)–C(9)	1.494 (5)	C(4)–C(8)	1.489 (4)
C(1)–S(1)	1.757 (3)	C(5)–S(2)	1.756 (3)
S(1)–C(10)	1.803 (4)	S(2)–C(6)	1.815 (3)
C(10)–C(11)	1.508 (5)	C(6)–C(7)	1.520 (5)

Table IV. Bond Angles (deg) for Complex **2**

I–Fe–N(1)	101.9 (1)	I–Fe–N(6)	102.1 (1)
I–Fe–N(3)	101.5 (1)	I–Fe–N(4)	101.7 (1)
N(1)–Fe–N(3)	79.6 (1)	N(6)–Fe–N(4)	80.1 (1)
N(1)–Fe–N(4)	156.1 (1)	N(6)–Fe–N(3)	156.2 (1)
N(3)–Fe–N(4)	92.9 (1)	N(1)–Fe–N(6)	97.7 (1)
Fe–N(1)–C(1)	113.0 (2)	Fe–N(6)–C(5)	111.4 (2)
Fe–N(3)–N(2)	117.1 (2)	Fe–N(4)–N(5)	116.8 (2)
Fe–N(3)–C(2)	125.8 (2)	Fe–N(4)–C(4)	126.8 (2)
N(1)–C(1)–N(2)	120.5 (2)	N(6)–C(5)–N(5)	121.1 (3)
C(1)–N(2)–N(3)	108.5 (2)	C(5)–N(5)–N(4)	108.7 (2)
N(2)–N(3)–C(2)	116.5 (2)	N(5)–N(4)–C(4)	116.0 (2)
N(3)–C(2)–C(3)	121.0 (3)	N(4)–C(4)–C(3)	120.5 (2)
N(3)–C(2)–C(9)	118.9 (2)	N(4)–C(4)–C(8)	119.3 (3)
C(3)–C(2)–C(9)	120.1 (3)	C(3)–C(4)–C(8)	120.2 (3)
N(1)–C(1)–S(1)	119.8 (2)	N(6)–C(5)–S(2)	120.3 (2)
N(2)–C(1)–S(1)	119.8 (2)	N(5)–C(5)–S(2)	118.6 (2)
C(1)–S(1)–C(10)	103.1 (1)	C(5)–S(2)–C(6)	101.0 (1)
S(1)–C(10)–C(11)	109.4 (3)	S(2)–C(6)–C(7)	108.9 (2)
C(2)–C(3)–C(4)	128.8 (3)		

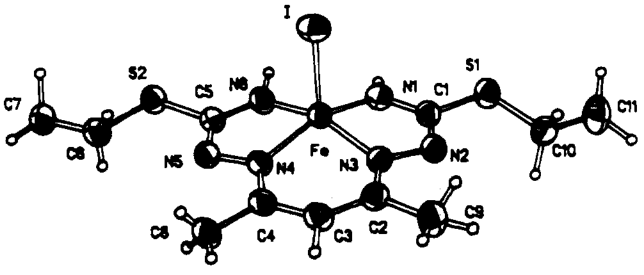


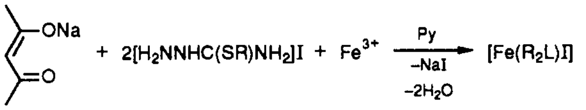
Figure 1. Molecular structure of complex **2**, showing the thermal vibration ellipsoids and the atom-numbering scheme.

Table V. Mössbauer Spectral Parameters[a]

complex	T, K	δ, mm s^{-1}	ΔE_Q, mm s^{-1}	Γ_l[b] = Γ_r,[c] mm s^{-1}
1	300	0.34	2.93	0.25
	80	0.42	2.94	0.27
2	300	0.35	2.94	0.38
	80	0.42	2.95	0.39
3	300	0.33	2.65	0.37
	195	0.41	2.90	0.29
	80	0.43	2.83	0.31
4	300	0.36	2.93	0.27
	195	0.42	2.96	0.29
	80	0.41	2.83	0.29

[a] The accuracy of the Mössbauer spectral parameters is ±0.04 mm s^{-1}. [b] Left line width. [c] Right line width.

acetylacetone and $Fe(NO_3)_3 \cdot 9H_2O$ in ethanol and in the presence of pyridine:



All the substances form as black-brown crystals well-soluble in chloroform, ethanol, and methanol. When heated in vacuo, they sublime without decomposition. In the mass spectra of these compounds there are peaks of the molecular ion $[Fe(R_2L)I]^+$, where R_2L is the triply deprotonated quadridentate ligand. These results are unexpected, as the salt-type compounds **1**–**4** sublime without changing their composition and, additionally, the central ion is present in a formal oxidation state +4. It is also important to note that five-coordinate iron(IV) have been established in the solid state only for the binuclear μ-carbido complex $[(TPP)Fe]_2C$[29] and macrocyclic tetraamido-*N* complex $[Et_4N][FeCl(\eta^4\text{-}1)]$.[30] These observations prompted us to carry out X-ray studies of **2**, as a typical representative of the complexes **1**–**4**.

Crystallographic Studies. In Figure 1 is presented the molecular structure of compound **2**. The structure of **2** consists of centrosymmetric dimeric units formed by establishing the N–H···I hydrogen bond. The distance N(6)–I is 3.845 Å (symmetry transformation for I: $1 - x$, $1 - y$, $1 - z$), and H(6)···I is 2.780 Å, the angle at H being 158°. Between the dimers there are only the van der Waals interactions; hence, such a compound can be regarded as a molecular complex. The square-pyramidal configuration is formed by the quadridentate ligand in the base (distances Fe–N(1), Fe–N(3), Fe–N(4), and Fe–N(6) are 1.884 (2), 1.900 (2), 1.905 (2), and 1.895 (3) Å, respectively) and I in the apical position (Fe–I = 2.578 (1) Å). The four nitrogen atoms, N(1), N(3), N(4), and N(6), are coplanar, the metal ion deviating from the plane to the I side by 0.389 Å.

It should be noticed that the Fe–N distance (average 1.896 Å) in **2** is significantly shorter in comparison to the Fe(III)–N distance in the pentacoordinated complexes with *S*-methyl-1,4-bis(salicylidene)isothiosemicarbazide (H_2Q), FeQCl[31] and the dimer $(FeQ)_2O$,[32] where this distance is 2.09 (5) and 2.102 (5) Å, respectively. As will be shown later, this shortening of the Fe–N bond length is related to the establishment of the $3d^4$ configuration of the iron atom. Analogous changes in the Fe–donor atom distances in comparison with those of the corresponding iron(III) complexes have been observed in a series of iron(IV) complexes with dithiocarbamates.[4]

The ligand $(C_2H_5)_2L^{3-}$ appears as a result of deprotonation of the two isothiosemicarbazide fragments and of the acetylacetone moiety. In the coordination with iron(IV), three metalla rings are formed: one six-membered (acetylacetone) and two five-membered (isothiosemicarbazide). The deviation of the Fe atom from the six-membered ring plane is 0.380 Å, and deviations from the planes of the two five-membered rings are 0.264 and 0.251 Å. In contrast to the nickel(II) complexes with 2,4-pentanedione bis(*S*-methylisothiosemicarbazone),[33] in which the methyl groups linked to the sulfur atoms (S(1) and S(2)) are oriented toward N(1) and N(6), the ethyl groups in **2** have an opposite orientation; i.e., they are oriented toward N(2) and N(5). This fact can be explained by the packing properties of the **2** molecules and by deprotonation of $H_3(C_2H_5)_2L$ occurring at the donor groups containing N(2) and N(5). This can yield a weak C–H···N interaction with the proton of the ethyl group. The sulfur atoms S(1) and S(2) deviate from the plane of the corresponding isothiosemicarbazide moiety by 0.110 and 0.111 Å, respectively. The deprotonation of the N(2) and N(5) atoms of the *S*-ethylisothiosemicarbazide fragments, $-NNHC(SC_2H_5){=}NH$, of the ligand leads to substantial changes of the bond lengths in it. Thus, the N(1)–C(1) and N(6)–C(5) distances are in average equal to 1.331 Å, whereas in the corresponding nickel-

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Table VI. Mass Spectral Data

	complex							
	1		**2**		**3**		**4**	
ion	m/z^a	I^b	m/z^a	I^b	m/z^a	I^b	m/z^a	I^b
$[M]^+$	454	26.3	482	58.4	510	25.0	538	28.1
$[M - I]^+$	327	100	355	100	383	100	411	100
$[M - I - RSH]^+$	279	12.3	293	19.5	307	7.7	321	4.7
$[M - I - (R\text{–}H)]^+$	313		327	15.6	341	5.0	355	4.2
$[M - I - NCSR]^+$	254	5.3	268	6.5	282	12.4	296	11.5
$[M - I - HN_2CSR]^+$	239	6.5	253	10.1	267	4.7	281	3.8
$[M - I - H_2N_2CSR]^+$	238	6.4	252	7.8	266	3.7	280	1.9
$[M - I - H_2N_3CSR]^+$	224	17.5	238	18.2	252	7.7	266	4.9
$[M - I - H_2N_2CSR - (R\text{–}H)]^+$	224	17.5	224	13.0	224	7.9	224	5.0
$[M - I - HN_3CSR - (R\text{–}H) - CH_3CN]^+$	183	24.6	183	24.7	183	10.0	183	8.3
$[CH_3CNFe]^+$	97	28.1	97	27.3	97	15.4	97	12.5
$[Fe]^+$	56	9.4	56	9.7	56	7.7	56	6.0
$[M - I]^{2+}$	163.5	6.3	177.5	1.7	191.5	1.4	205.5	0.6

[a] Values m/z are given for ^{56}Fe, ^{32}S, and ^{127}I. [b] In %.

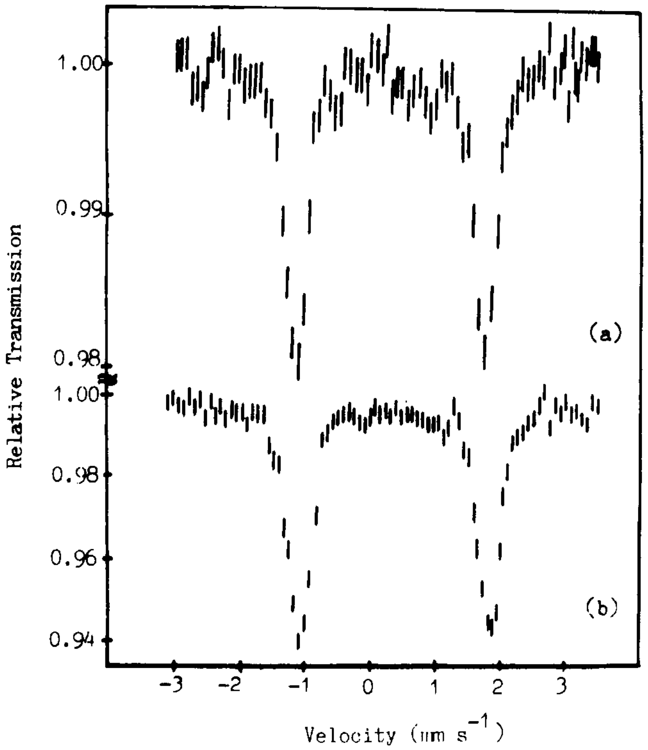

Figure 2. Mössbauer spectra of complex **2** recorded at (a) 300 and (b) 80 K. The number of counts per velosity point is approximately equal to 416 000 (300 K) and 142 900 (80 K).

(II) complexes these distances are 1.298 Å.[33] On the other hand, the N(2)–C(1) and N(5)–C(5) distances in **2** and in the mentioned nickel(II) compound are 1.312 and 1.337 Å, respectively. The distances N(2)–N(3) (1.368 (3) Å) and N(4)–N(5) (1.361 (3) Å) (average 1.365 (3) Å) are significantly shorter compared to that in the nickel(II) complex (1.401 (3) Å), which suggests a higher degree of delocalization of electron density over the ligand of the iron(IV) complex as a whole. In the six-membered ring, full delocalization of the π-electrons is observed. The N–C and C–C distances in this ring are close to those of other π-conjugated systems.[34]

Magnetic Properties and Mössbauer Spectra. The measurement of magnetic susceptibility of complexes **1–4** gave the magnetic moments of 2.9–3.0 μ_B at room temperature, corresponding to the presence of two unpaired electrons. The Mössbauer spectra (Table V) are of doublet form with the identical peak intensities and approximately equal line widths. The Mössbauer spectra of [Fe(Et$_2$L)I] at 300 (1) and 80 K (2) are given in Figure 2. The isomer shifts δ (relative to sodium nitroprusside) are in the range 0.33–0.36 mm s^{-1} at room temperature. These values suggest the presence of an oxidation state of iron higher than +3.[13,30,35,36] An increase in δ (at 80 K; see Table V), what may be attributable to, at least in part, a second-order Doppler shift arising from lattice effects, is observed. The value of the quadrupole splitting ΔE_Q in the Mössbauer spectra of the iron-containing complexes is determined by the asymmetric distribution of the ionic charge surrounding the Mössbauer atom and by the incompletely filled 3d and 4p iron AO's:[35]

$$\left(\frac{V_{zz}}{e}\right)_{\text{val}} = {}^4/_7(1 - R)_{3d}\,\langle r^{-3}\rangle_{3d}[N_{x^2-y^2} - N_{z^2} + N_{xy} - {}^1/_2(N_{xz} + N_{yz})] + {}^4/_5(1 - R)_{4p}\langle r^{-3}\rangle_{4p}[-N_{pz} + {}^1/_2(N_{px} + N_{py})] \quad (1)$$

$$(V_{zz})_{\text{lat}} = (1 - \gamma_\infty)\sum_{i=1}^{n} q_i \frac{3z_i^2 - r_i^2}{r_i} \quad (2)$$

Here $(1 - R)$ and $(1 - \gamma_\infty)$ are the Sternheimer factors equal to 0.68 and 12, respectively, $\langle r^{-3}\rangle_{3d}$ and $\langle r^{-3}\rangle_{4p}$ are the average values of radial coordinates of the 3d and 4p electrons, r_i is the radial coordinate of the ith atom, q_i is the charge on the ith atom, z_i is the Cartesian coordinate of the ith atom, and N is the electronic population of the given AO. It should be noticed that, in the first approximation, the contribution of the asymmetry $\langle \eta V_{zz}\rangle$, $(V_{zz})_{\text{lat}}$, and the asymmetrically filled 4p iron AO in $(V_{zz}/e)_{\text{val}}$ to the electronic configuration of complexes **1–4** can be neglected. As a result, the gradient of the electric field in the region of the Mössbauer nucleus will be determined by the imbalance of the electronic density on the valence 3d AO's of the iron.

The symmetry of the closest surroundings of the central ion in the given complexes is close to D_{4h}, and degeneracy of the t_{2g} orbital is lifted.

On comparison of the magnetic data and Mössbauer spectral data of compounds **1–4** with the literature data,[5,6,8,9,13,30,36] it can be concluded that the presented data correspond to a 3d^4 configuration in the ground-state $S = 1$. The ΔE_Q values for the Mössbauer spectra of **1–4** are close to those for [Fe(Diars)$_2$X$_2$]BF$_4$. This fact permits to one suppose that ΔE_Q values (for **1–4**) have the same sign, i.e. $\Delta E_Q > 0$.[9]

On the basis of data presented here, it can be concluded that the electronic configuration of the central ion in complexes **1–4**

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is $d_{xy}^2 d_{xz} d_{yz}$. As the ΔE_Q values are almost independent of temperature (Table V), the energy gap between the d_{xy} on the one hand and d_{xy}, d_{yz} AO's on the other is significantly greater than kT.

Mass Spectra. The mass spectra of all complexes (Table VI) are characterized by strong molecular ion peaks, with the strongest peak belonging to the $[M - I]^+$ ion. The presence of $[M]^+$ and also $[M - I]^{2+}$ indicates a high stability of **1**–**4** toward electron impact. One of the basic fragmentation routes of $[M]^+$ involves the cleavage of I, which causes a decrease in the oxidation state of the central ion to +3. Further fragmentation of the $[M - I]^+$ ion proceeds on account of the isothiosemicarbazide residues.

Conclusion

A novel class of iron complexes based on *S*-alkylisothiosemicarbazides, in which the central atom is in an unusual oxidation state +4, has been obtained via a template procedure. As the starting salt was iron(III) nitrate, it can be supposed that the oxidation of iron(III) to iron(IV), in the presence of the template ligand formed, is accomplished by I_2 produced in the reaction of Fe(III) and I^-. The Fe(IV) resulting from this redox process is stabilized in the form of the $[Fe(R_2L)I]$ complex. It can be supposed that the unusual route of the redox process observed in the preparation of **1**–**4** is facilitated by a number of factors such as the ability of the organic ligand to release three protons in the process of the complex formation and the highly conjugated nature of the ligand exhibiting inherent flexibility of the electronic system as a whole, as well as by the potential ability of the ligand to stabilize a high oxidation state of the central atom.

Acknowledgment. We are indebted to Miss M. S. Birka for recording the Mössbauer spectra.

Supplementary Material Available: Mössbauer spectra of compound **1** at 300 and 80 K (Figure S1a,b), of compound **3** at 300, 195, and 80 K (Figure S2a–c), and of compound **4** at 300, 195, and 80 K (Figure S3a–c), a view of the unit cell packing diagram for compound **2** (Figure S4), anisotropic temperature factors for all non-hydrogen atoms (Table SI), and raw mass spectral data for complexes **1**–**4** (Table SIII) (8 pages); a listing of observed and calculated structure factors (Table SII) (21 pages). Ordering information is given on any current masthead page.