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Crown Thioether Chemistry of Iron(II/III). Synthesis and Characterization of Low-Spin Bis(1,4,7-trithiacyclononane)iron(III) and Crystal Structure of $[Fe^{II}([9]aneS_3)([9]aneS_3(O))](ClO_4)_2 \cdot 2NaClO_4 \cdot H_2O$

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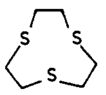
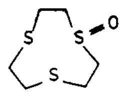
The oxidation of purple $[FeL_2]^{2+}$, where L represents the cyclic crown thioether 1,4,7-trithiacyclononane ($C_6H_{12}S_3$), with PbO_2 in 1 M sulfuric acid yielded green $[FeL_2]^{3+}$, which has been isolated as $[FeL_2](PF_6)_3$ and characterized by magnetic susceptibility measurements and its electronic and Mössbauer spectra to contain a Jahn-Teller-distorted low-spin $[Fe^{III}S_6]^{3+}$ core. $[FeL_2]^{3+}$ is a strong one-electron oxidant ($E_{1/2}$ = +0.98 V vs ferrocenium/ferrocene in acetonitrile), which oxidizes Cl^- and H_2O_2. In contrast, oxidation of $[FeL_2]^{2+}$ in aqueous solution with $Na_2S_2O_8$ afforded upon addition of $NaClO_4$ two crystalline materials: mixed crystals of $[FeL_2][FeLL^1](ClO_4)_4$ and $[Fe^{II}LL^1](ClO_4)_2 \cdot 2NaClO_4 \cdot H_2O$, where L^1 represents 1,4,7-trithiacyclononane 1-oxide. Electronic spectra, ^1H NMR measurements, and a single-crystal X-ray diffraction study of the latter material showed that the iron center is still in the oxidation state +II, is low spin, and is coordinated to one 1,4,7-trithiacyclononane and its oxidized form 1,4,7-trithiacyclononane 1-oxide, forming a pseudooctahedral $[FeS_6]^{2+}$ core. $[FeLL^1](ClO_4)_2 \cdot 2NaClO_4 \cdot H_2O$ crystallizes in the triclinic system, space group $P\bar{1}$, with a = 10.145 (7) Å, b = 12.323 (6) Å, c = 12.465 (6) Å, α = 82.91 (4)°, β = 86.09 (4)°, γ = 83.16 (5)°, and Z = 4. These results show that oxidation reactions of coordinated thioether complexes of iron(II) may be either at the metal or at the ligand depending on the nature of the oxidant used.

Introduction

The coordination chemistry of crown thioether ligands is presently being actively investigated in several laboratories. Contrary to the common experience that thioethers are rather poor ligands for the coordination of transition metals,[23] the picture begins to emerge that this is not the case for at least the macrocycles 1,4,7-trithiacyclononane (L) and 1,4,7,10,13,16-hexathiacyclooctadecane (L^2). A number of homoleptic complexes containing, in general, a later transition metal in a relatively low oxidation state (≤II; soft acids) have been synthesized and characterized by X-ray crystallography.


L ; [9]aneS$_3$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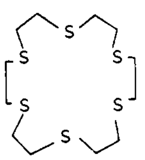
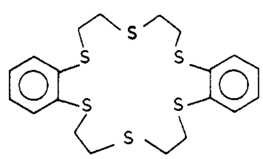

L^2 ; [18]aneS$_6$


L^3

Homoleptic, six-coordinate complexes containing crown thioether ligands of Co(II),[4-7] Ni(II),[4,8,9] Cu(II),[4,10] Pd(II),[11-13] Pt(II),[13] Ag(I),[14] and Ru(II)[15] have been isolated, all of which contain a MS_6 core. Two Cu(I) thioether complexes of L_2 have also been reported and structurally characterized;[10,16] we have recently reported the structure of Cu^ILI.[14]

In contrast, the coordination chemistry of the earlier first-row transition metals (hard acids) with thioethers has received much less attention in the past because of the presumed instability of the metal-thioether bonds. Only recently two such complexes of iron(II) have been reported, $[FeL_2]^{2+}$ [17] and $[FeL^3]Br_2$.[18] The former has been characterized by X-ray crystallography.

A further very interesting aspect of this chemistry is the discovery that the macrocyclic thioether 1,4,7-trithiacyclononane stabilizes in some instances quite unusual, relatively high oxidation states of some transition-metal centers. Schröder and co-workers[19]

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have shown that it is possible to electrochemically oxidize $[PdL_2]^{2+}$ and $[PtL_2]^{2+}$ complexes to the homoleptic monomeric Pd^{III} and Pt^{III} complexes. The former has been isolated as a crystalline material and characterized by X-ray crystallography.[20] We have previously shown that $[CoL_2]^{3+}$—a strong one-electron oxidant—is stable in solution and in the solid state.[5]

During our investigations of the properties of the low-spin $[FeL_2]^{2+}$ complex it became apparent[17] that it is possible to reversibly oxidize this octahedral $[FeS_6]^{2+}$ species electrochemically in acetonitrile at the very positive redox potential of +0.982 V vs the ferrocenium (Fc^+)/ferrocene (Fc) reference electrode. At that time it was not clear whether this one-electron process corresponded to a metal-centered oxidation of iron(II) to iron(III) or whether ligand oxidation had occurred, yielding a coordinated sulfonium ion. We have now been able to carry out this oxidation chemically in 1 M sulfuric acid using PbO_2 as oxidant. We have isolated the green complex $[FeL_2](PF_6)_3$, which we will show to contain a genuine low-spin iron(III) center.

If, on the other hand, sodium peroxodisulfate was used as oxidant for $[FeL_2]^{2+}$, ligand oxidation was observed and no formation of iron(III) was detected. The species formed has been characterized as the $[FeLL^1]^{2+}$ complex, where one 1,4,7-trithiacyclononane ligand has been oxidized to 1,4,7-trithiacyclononane 1-oxide (L^1). The sulfoxide group is S-coordinated to an iron(II) center. The chemistry, spectroscopic properties, and X-ray structure determination of $[FeLL^1](ClO_4)_2\cdot 2NaClO_4\cdot H_2O$ will be reported here.

Experimental Section

Preparation of Compounds. 1,4,7-Trithiacyclononane (L) was prepared by Sellmann's method.[21] $MoL(CO)_3$[21,22] and $[FeL_2](PF_6)_2$[17] were prepared as described in the literature. For the present purposes the latter was converted to the perchlorate salt. *Caution*! $[FeL_2](ClO_4)_2$ and especially $[FeL_2](ClO_4)_3$ are sensitive to shock and heat; they, like all perchlorates, should be prepared only in small quantities and handled with extreme care as they explode violently and uncontrollably.

$[FeL_2](PF_6)_3$. $[FeL_2](ClO_4)_2$ (0.2 g, 0.33 mmol) was dissolved in 10 mL of 1 M sulfuric acid, and PbO_2 (0.2 g, 0.84 mmol) was added with stirring at room temperature. After 10 min the green solution was filtered. Addition of $NaPF_6$ (2 g) initiated the rapid precipitation of green microcrystals, which were collected by filtration, washed with dry ether, and dried in vacuo; yield 0.21 g. Anal. Calcd for $C_{12}H_{24}S_6P_3F_{18}$: C, 16.93; H, 2.84; S, 22.60. Found: C, 17.2; H, 3.0; S, 23.0. IR (KBr, cm^{-1}): 3000 (w), 2950 (w), 2920 (w), 1440 (m), 1400 (s), 1285 (vw), 1270 (vw), 1250 (vvw), 1160 (w), 1125 (vw), 1110 (vw), 1080 (m), 1000 (vvw), 935 (w), 910 (w), 870 (sh, s), 825 (vvs), 725 (m), 710 (sh), 650 (vw), 610 (w), 545 (vs), 480 (vw), 455 (vw).

$[FeLL^1](ClO_4)_2\cdot 2NaClO_4\cdot H_2O$. A solution of $[FeL_2](ClO_4)_2$ (0.2 g, 0.33 mmol) and $Na_2S_2O_8$ (1.5 g, 7 mmol) in water (60 mL) was heated to 60 °C for 1 h, after which time the purple color of the original solution had changed to orange. Upon cooling of this solution to 10 °C for a few hours orange microcrystals of $[FeLL^1](S_2O_8)\cdot H_2O$ could be isolated. (Anal. Calcd for $C_{12}H_{26}FeO_{10}S_8$: C, 22.43; H, 4.08; S, 39.91. Found: C, 22.6; H, 4.2; S, 39.5.) If, on the other hand, $NaClO_4\cdot H_2O$ (1 g) was added to the above warm solution, orange-red crystals precipitated at 20 °C, which were collected by filtration. This material was shown by ^1H NMR spectroscopy, cyclic voltammetry, and an X-ray diffraction study to consist of mixed crystals of $[FeL_2][FeLL^1](ClO_4)_4$ containing unreacted $[FeL_2]^{2+}$ and $[FeLL^1]^{2+}$ cations in equimolar amounts and ClO_4^-. If the mother liquid was then allowed to stand in an open vessel at room temperature for 2 days, orange-brown crystals of $[FeLL^1](ClO_4)_2\cdot 2NaClO_4\cdot H_2O$ suitable for an X-ray diffraction study precipitated. All spectroscopic measurements were performed with this material exclusively. Anal. Calcd for $C_{12}H_{26}Cl_4FeNa_2O_{18}$: C, 16.11; H, 2.93; S, 21.51. Found: C, 16.5; H, 3.0; S, 21.2. IR (KBr, cm^{-1}): 3520 (m), 3420 (sh), 3380 (m), 3200 (sh), 2960 (w), 2910 (w), 2900 (sh), 1640 (w), 1620 (m), 1600 (m), 1430 (m), 1395 (m), 1100 (vs, b), 930 (sh), 925 (w), 900 (w), 830 (w), 815 (w), 682 (w), 660 (vw), 620 (s), 610 (s), 590 (m). The hexafluorophosphate salt exhibits a band at 1090 cm^{-1}, which we assign to the ν(S=O) stretching mode.

Oxidation of $LMo(CO)_3$ and 1,4,7-Trithiacyclononane. $LMo(CO)_3$ (0.3 g, 1 mmol) was refluxed in 30 mL of 30% H_2O_2 for 10 min. The resulting clear yellow solution was allowed to stand at room temperature for a few hours. Colorless crystals of 1,4,7-trithiacyclononane 1,1,4,4,7,7-hexaoxide[23] precipitated, which were collected by filtration with ether and air-dried; yield 90%. Anal. Calcd for $C_6H_{12}O_6S_3$: C, 26.27; H, 4.40; S, 34.33. Found: C, 26.3; H, 4.4; S, 34.10. IR (KBr disk, cm^{-1}): 2960 (m), 2920 (m), 1450 (m), 1430 (m), 1410 (vw), 1350 (ms), 1310 (s), 1270 (ms), 1205 (vw), 1190 (vw), 1170 (vw), 1150 (ms), 1130 (s), 1120 (s), 1040 (vvw), 1030 (vw), 940 (w), 910 (w), 860 (w), 840 (vvw), 790 (s), 730 (w), 660 (vvw), 620 (vvw), 505 (m), 445 (ms).

The same product was obtained by boiling 1,4,7-trithiacyclononane in 30 mL of 30% H_2O_2 for 2 min. From the clear solution colorless crystals precipitated out upon cooling; yield 90%. The compound is insoluble in all common solvents.

Table I. Experimental Details of the X-ray Diffraction Study of $[FeLL^1](ClO_4)_2\cdot 2NaClO_4\cdot H_2O$

mol wt	894.34
a, Å	10.145 (7)
b, Å	12.323 (6)
c, Å	12.465 (6)
α, deg	82.91 (4)
β, deg	86.09 (4)
γ, deg	83.16 (5)
V, Å^3	1533.2
Z	4
space group	$P\bar{1}$
D_{calcd}, g cm^{-3}	1.93
cryst dimens, mm^3	0.30 × 0.33 × 0.60
instrument	AED II (Siemens)
radiation	Mo Kα (graphite monochromatized)
2θ limits, deg	3–60
scan type	ω
octant	$\pm h,\pm k,l$
μ, cm^{-1}	13.4
abs cor	empirical
max and min transmission coeff	1.0, 0.78
obsd data	9010
unique data ($I \geq 2\sigma(I)$)	6267
no. of refined params	446
shift/esd	0.02 (mean), 0.3 (max)
final *R*	0.058
final R_w	0.056
R_{merge}	0.04
final GOF	4.3

Physical Measurements. Electronic spectra were recorded with quartz cuvettes on a Perkin-Elmer Lambda 9 spectrophotometer; infrared spectra were obtained on KBr disks with a Beckman Acculab 10 spectrophotometer. Magnetic susceptibilities of powdered samples were measured by the Faraday method (Sartorius microbalance, Bruker B-E10 C8 research magnet and B-VT 1000 automatic temperature control) in the temperature range 110–298 K. Diamagnetic corrections were applied in the usual manner with use of Pascal's constants.

Electrochemical measurements were performed with a Princeton Applied Research Model 175 programmer, Model 173 potentiostat, and Model 179 digital coulometer and a Kipp & Zonen xy recorder (Model BD 90) on acetonitrile solutions that were 0.1 M in $[n\text{-}Bu_4N]PF_6$. A standard three-electrode cell was employed with a platinum-button working electrode, a platinum-wire auxiliary electrode, and a Ag/AgCl reference electrode (saturated LiCl/ethanol). Potentials are referenced vs. the ferrocenium/ferrocene couple as internal standard. Cyclic voltammograms were recorded at scan rates from 20 to 500 mV s^{-1}; the concentration of the electroactive component was 5×10^{-4} M. Mössbauer measurements were performed with a conventional setup in the constant-acceleration mode using a 50-mCi $^{57}Co/Rh$ source. Low sample temperatures were achieved in a Model MD 306 He-bath cryostat equipped with a Model 3120 temperature controller, both from Oxford Instruments. The data were collected with a Model ND66 multichannel analyzer (Nuclear Data GmbH). The spectra were analyzed by a least-squares fit procedure using Lorentzian line shape, and calibration was achieved with respect to α-Fe at ambient temperature.

^1H and ^{13}C NMR spectra were recorded on a Bruker AM-400 spectrometer equipped with a 5-mm dual probe at ambient temperature, in D_2O solutions. Experimental parameters: ^1H, 400.13 MHz, 4000-Hz sweep width, 1.5-μs pulse width (20°), HDO (δ = 4.66) as internal standard; ^{13}C, 100.61 MHz, 25-kHz sweep width, 7.5-μs pulse width (90°).

X-ray Structure Determination. Crystallographic details are summarized in Table I. The crystal was mounted on a glass capillary and centered on an AED II (Siemens) automatic diffractometer, and the cell dimensions and orientation matrix were determined by least-squares refinement of the setting angles of 26 reflections ($8 < 2\theta < 40°$) at ambient temperature. Data were corrected for Lorentz and polarization effects, and an empirical absorption correction was performed. The SHELXTL suite of crystallographic programs was used for all calculations.

Table II. Atomic Coordinates ($\times 10^4$) of $[FeLL^1](ClO_4)_2 \cdot 2NaClO_4 \cdot H_2O$

atom	x	y	z	occupancy
Fe1	0	0	0	0.5
Fe2	5000	5000	5000	0.5
S1	146 (1)	322 (1)	1687 (1)	1
S2	1504 (1)	1194 (1)	−552 (1)	1
S3	1657 (1)	−1381 (1)	215 (1)	1
O1	−1050 (6)	677 (5)	2402 (6)	0.5
C1	1326 (5)	1316 (5)	1652 (4)	1
C2	1443 (6)	1997 (4)	575 (4)	1
C3	3129 (5)	366 (4)	−400 (5)	1
C4	3047 (5)	−805 (4)	−541 (5)	1
C5	2107 (6)	−1434 (5)	1627 (4)	1
C6	1028 (6)	−945 (5)	2323 (5)	1
S4	3210 (1)	4669 (1)	6126 (1)	1
S5	5069 (1)	3338 (1)	4492 (1)	1
S6	3638 (1)	5648 (1)	3650 (1)	1
O2	6272 (6)	2532 (5)	4428 (6)	0.5
C11	3320 (5)	3173 (4)	6281 (4)	1
C12	3688 (5)	2708 (4)	5239 (4)	1
C13	4546 (5)	3578 (4)	3115 (4)	1
C14	3385 (5)	4456 (4)	2980 (4)	1
C15	2067 (5)	5918 (4)	4393 (4)	1
C16	8220 (4)	4974 (4)	4717 (4)	1
Cl1	−12 (1)	4376 (1)	8341 (1)	1
O11	1182 (4)	4287 (4)	8873 (4)	1
O12	−283 (5)	5416 (4)	7816 (5)	1
O13	8934 (5)	4080 (5)	9040 (5)	1
O14	10156 (6)	3628 (6)	7559 (4)	1
Cl2	4714 (1)	3546 (1)	9434 (1)	1
O21	3831 (4)	3718 (4)	381 (3)	1
O22	6073 (4)	3533 (4)	9655 (4)	1
O23	4535 (4)	2543 (3)	9050 (4)	1
O24	4365 (4)	4452 (3)	8629 (3)	1
Cl3	378 (1)	1747 (1)	4673 (1)	1
O31	646 (5)	2700 (3)	3976 (4)	1
O32	1095 (5)	814 (4)	4296 (4)	1
O33	771 (6)	1820 (6)	5699 (4)	1
O34	−991 (4)	1646 (4)	4740 (4)	1
Cl4	4798 (2)	78 (1)	3188 (1)	1
O41	4474 (7)	358 (9)	2109 (6)	0.5
O42	4097 (20)	583 (25)	3968 (21)	0.5
O43	4406 (14)	−898 (8)	3094 (15)	0.5
O44	6054 (7)	−29 (9)	3384 (7)	0.5
O45	−5565 (10)	865 (8)	2330 (8)	0.5
O46	−5956 (10)	−692 (12)	3745 (10)	0.5
O47	−3770 (11)	−351 (13)	3051 (9)	0.5
O48	−5269 (33)	860 (19)	3886 (20)	0.5
Na1	7517 (2)	4442 (2)	536 (2)	1
Na2	7259 (4)	643 (4)	4724 (4)	0.5
Na3	7748 (5)	309 (4)	4276 (5)	0.5
O_w	8166 (5)	3156 (4)	2058 (4)	1

Table III. Selected Bond Distances (Å) and Angles (deg) of the Two Independent Cations $[FeLL^1]^{2+}$ in $[FeLL^1](ClO_4)_2 \cdot 2NaClO_4 \cdot H_2O$

cation I		cation II	
Fe1–S1	2.205 (1)	Fe2–S4	2.263 (1)
Fe1–S2	2.260 (1)	Fe2–S5	2.209 (1)
Fe1–S3	2.250 (1)	Fe2–S6	2.258 (1)
S1–O1	1.511 (7)	S5–O2	1.484 (6)
S1–C1	1.807 (6)	S5–C12	1.826 (5)
S1–C6	1.823 (6)	S5–C13	1.810 (5)
S2–C2	1.810 (6)	S4–C11	1.821 (5)
S2–C3	1.841 (5)	S4–C16	1.828 (5)
S3–C4	1.809 (6)	S6–C14	1.829 (5)
S3–C5	1.839 (6)	S6–C15	1.805 (5)
C1–C2	1.499 (7)	C11–C12	1.491 (7)
C3–C4	1.488 (8)	C13–C14	1.505 (7)
C5–C6	1.469 (8)	C15–C16	1.502 (7)
S2–Fe1–S1	89.8 (1)	S5–Fe2–S4	89.7 (1)
S3–Fe1–S1	90.0 (1)	S6–Fe2–S4	89.9 (1)
S1′–Fe1–S1	180.0 (1)	S4′–Fe2–S4	180.0 (1)
S2′–Fe1–S1	90.3 (1)	S5′–Fe2–S4	90.3 (1)
S3′–Fe1–S1	90.0	S6′–Fe2–S4	90.2 (1)
O1–S1–Fe1	122.9 (3)	O2–S5–Fe2	125.6 (3)
C1–S1–Fe1	106.6 (2)	C12–S5–Fe2	106.3 (2)
C6–S1–Fe1	103.3 (2)	C13–S5–Fe2	104.5 (2)
C1–S1–O1	108.4 (3)	C12–S5–O2	111.3 (3)
C6–S1–O1	109.7 (3)	C13–S5–O2	103.6 (3)
C6–S1–C1	103.7 (3)	C13–S5–C12	103.2 (2)

Atomic scattering factors, including anomalous dispersion, were taken from ref 24.

The structure was solved via conventional Patterson and Fourier syntheses. The structure was refined by use of block-cascade least-squares methods, with anisotropic temperature factors for all non-hydrogen atoms. The quantity minimized was $\sum w(|F_o| - |F_c|)^2$, where the weights w were taken as $1/\sigma(F)^2$. The contribution of hydrogen atoms bound to carbon was introduced in calculated positions (C–H = 0.96 Å, sp^3-hybridized carbon atoms). These hydrogen atoms were assumed to have isotropic thermal motion ($U = 0.048$ Å^2). The final values of $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ are given in Table I. The highest peak in the final difference Fourier map had an electron density of 0.5 e/Å^3. Final positional parameters are given in Table II, and selected bond lengths and angles appear in Table III.

In $[FeLL^1](ClO_4)_2 \cdot 2NaClO_4 \cdot H_2O$ one perchlorate anion and the sodium cation coordinated to this anion were disordered and were readily modeled with two molecules, each with a site occupancy of 0.5 for Na2, Na3, O41, O42, O43, O44, O45, O46, O47, and O48 and anisotropic temperature factors. In addition, the complex cation shows a disorder. The two independent iron(II) centers are each located on a crystallographic center of symmetry, (0, 0, 0) and ($^1/_2$, $^1/_2$, $^1/_2$), and consequently, the sulfoxide oxygen atom of one coordinated macrocycle of each cation has a site occupancy of 0.5. Refinement of this factor converged at a value of 0.48 and was set at 0.5 in the final refinement cycle.

The X-ray diffraction study of a mixed crystal of $[FeL_2][FeLL^1](ClO_4)_4$ was performed analogously. Experimental details and results are available as supplementary material.

Results and Discussion

Syntheses of Complexes. Oxidation of purple, octahedral bis(1,4,7-trithiacyclononane)iron(II) in 1 M sulfuric acid with PbO_2 at ambient temperature yields a green solution. Addition of $NaClO_4$ or $NaPF_6$ affords the green solids $[FeL_2](ClO_4)_3$ and $[FeL_2](PF_6)_3$. The former material is extremely sensitive to shock and/or heat and explodes violently. $[Fe^{III}L_2]^{3+}$ is a very strong one-electron oxidant; the salts were found to decompose slowly within days even when stored under a dry argon atmosphere. Aqueous solutions of this cation ($\sim 10^{-3}$ M) are only stable for ~5 min at pH 6 and approximately 1 h at pH 1. It oxidizes water (or OH^-), producing $[FeL_2]^{2+}$. We are at present examining this reaction in more detail. $[Fe^{III}L_2]^{3+}$ also oxidizes chloride and H_2O_2 according to eq 1 and 2.

$$2[FeL_2]^{3+} + 2Cl^- \rightarrow Cl_2 + 2[FeL_2]^{2+} \qquad (1)$$

$$2[FeL_2]^{3+} + H_2O_2 \rightarrow O_2 + 2[FeL_2]^{2+} + 2H^+ \qquad (2)$$

When a purple aqueous solution of $[FeL_2]^{2+}$ at 60 °C is treated with sodium peroxodisulfate, which is also a strong oxidant, the solution does not become green but orange, instead. Addition of $NaClO_4$ affords an orange, diamagnetic material that contains unreacted $[FeL_2]^{2+}$ and $[FeLL^1]^{2+}$, as is deduced from its electrochemistry and ^1H NMR spectrum, $[FeL_2][FeLL^1](ClO_4)_4$. From the mother liquid an orange-brown material, which we analyzed to be $[Fe^{II}LL^1](ClO_4)_2 \cdot 2NaClO_4 \cdot H_2O$, slowly crystallized (see below). When this perchlorate salt is converted to the hexafluorophosphate salt, a new band at 1090 cm^{-1} in the infrared spectrum is observed, which indicates the presence of an S-coordinated sulfoxide.[25] This band is not present in either $[FeL_2]^{2+}$ or $[FeL_2]^{3+}$.

The sulfoxide thioether ligand in $[FeLL^1]^{2+}$ is reduced in aqueous solution with zinc, affording quantitatively $[FeL_2]^{2+}$.

Thus, depending on the nature of the oxidant used, a metal-centered one-electron oxidation of $[Fe^{II}L_2]^{2+}$ to give $[Fe^{III}L_2]^{3+}$

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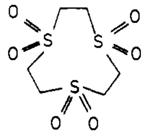
(24) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.

(25) Cotton, F. A.; Francis, R.; Horrocks, W. D. *J. Phys. Chem.* **1960**, *64*, 1534.

is observed or, alternatively, ligand oxidation occurs, affording a six-coordinate iron(II) species, $[Fe^{II}LL^1]^{2+}$, which contains one coordinated 1,4,7-trithiacyclononane 1-oxide ligand and one 1,4,7-trithiacyclononane ligand.

The formation of these different oxidation products may be rationalized as follows: PbO_2, which is a 2e oxidant, undergoes simple electron transfer: one electron each from two $[Fe^{II}L_2]^{2+}$ moieties ($[FeL_2]^{2+}$ is stable in 1 M H_2SO_4). $[S_2O_8]^{2-}$, which also formally acts as a 2e oxidant, concomitantly transfers an oxygen atom (the oxygen atom of the sulfoxide may come from $[S_2O_8]^{2-}$ or water). On the other hand, $[Co^{II}L_2]^{2+}$ is quantitatively oxidized by $[S_2O_8]^{2-}$ to $[Co^{III}L_2]^{3+}$ without any detectable ligand oxidation.[5] Thus, factors governing the oxidation of coordinated-thioether versus metal-centered oxidations remain to be delineated as more experimental data become available. It is of interest in this context that Nonoyama et al.[26] have reported that 1-thia-4,7-diazacyclononane may be oxidized with hypobromite, OBr^-, to give 1-thia-4,7-diazacyclononane 1-oxide. The sulfoxide group was found to be O-coordinated in bis complexes of Co^{II}, Cu^{II}, and Ni^{II}.

Interestingly, when $LMo(CO)_3$ is treated with 30% H_2O_2, a yellow solution is obtained from which colorless crystals of 1,4,7-trithiacyclononane 1,1,4,4,7,7-hexaoxide



precipitate slowly. This compound has been previously obtained by oxidation of 1,4,7-trithiacyclononane with MnO_4^- in acidic aqueous solution.[23] In the infrared spectrum (KBr disk) two groups of S=O stretching frequencies are observed at 1350, 1310, and 1280 cm^{-1} (ν_{as}(S=O)) and at 1150, 1130, and 1120 cm^{-1} (ν_s(S=O)). The same product is obtained by reacting the uncoordinated ligand with 30% H_2O_2. It is likely that the reaction of $LMo(CO)_3$ with H_2O_2 proceeds via oxidative decarbonylation of the molybdenum center with concomitant ligand dissociation and subsequent oxidation of the free ligand.

Electrochemistry. In the cyclic voltammogram off $[FeL_2](ClO_4)_2$ measured in acetonitrile containing 0.1 M $[n\text{-}Bu_4N]PF_6$ as supporting electrolyte, a reversible one-electron wave at +0.98 V vs. ferrocenium (Fc^+)/ferrocene (Fc) in the potential range +1.5 to −1.8 V (vs. Fc^+/Fc) had been observed.[17] Since the free ligand 1,4,7-trithiacyclononane exhibits under identical experimental conditions an irreversible oxidation peak at +0.99 V vs. Fc^+/Fc, it was at that time argued that oxidation of $[FeL_2]^{2+}$ is not necessarily a metal-centered oxidation leading to $[Fe^{III}L_2]^{3+}$ but a reversible one-electron oxidation of the coordinated ligand. The chemical oxidation of $[FeL_2]^{2+}$ by PbO_2 yields green $[Fe^{III}L_2](PF_6)_3$—a genuine low-spin iron(III) complex as was judged by its magnetic properties and Mössbauer spectrum (see below). The cyclic voltammogram of $[FeL_2](PF_6)_3$ in 0.1 M $[n\text{-}Bu_4N](PF_6)$/acetonitrile was found to be identical with that of $[FeL_2](ClO_4)_2$; a reversible one-electron-transfer reaction occurs at $E_{1/2}$ = +0.98 V vs. Fc^+/Fc.

These experiments have demonstrated unambiguously an electrochemical metal-centered one-electron oxidation of $[FeL_2]^{2+}$. Interestingly, the redox potential of the analogous $[RuL_2]^{3+/2+}$ couple[15] has been observed at a much more positive potential, $E_{1/2}$ = +1.41 V vs. Fc^+/Fc, indicating an even more pronounced stabilization of the Ru(II) species by two 1,4,7-trithiacyclononane ligands. Thus, this crown thioether has considerable π-acceptor properties.

The reaction of $[FeL_2]^{2+}$ with $Na_2S_2O_8$ in aqueous solution yielded upon addition of $NaClO_4$ two products: the immediately precipitating orange crystalline material $[FeL_2][FeLL^1](ClO_4)_4$ and orange-brown crystals of $[FeLL^1](ClO_4)_2 \cdot 2NaClO_4 \cdot H_2O$, which crystallized slowly from the mother liquid. The former material consists of mixed crystals that contain unreacted $[FeL_2](ClO_4)_2$ and $[FeLL^1](ClO_4)_2$ in equimolar amounts. This is nicely seen in the cyclic voltammogram measured in acetonitrile with 0.1 M $[n\text{-}Bu_4N]PF_6$ as supporting electrolyte (Figure 1). Two reversible one-electron-transfer processes are observed at $E_{1/2}$ = 0.98 and 1.32 V vs. Fc^+/Fc. The former is assigned to the couple $[FeL_2]^{3+/2+}$, whereas the latter process corresponds to the reversible one-electron oxidation of $[FeLL^1]^{2+}$. The cyclic voltammogram of $[FeLL^1](ClO_4)_2 \cdot 2NaClO_4 \cdot H_2O$ in 0.1 M $[n\text{-}Bu_4N]PF_6$/acetonitrile exhibits only one reversible one-electron wave at 1.32 V vs. Fc^+/Fc. Thus, cyclic voltammetry is well-suited to test the purity of the crystalline materials obtained by the above oxidation of $[FeL_2]^{2+}$.

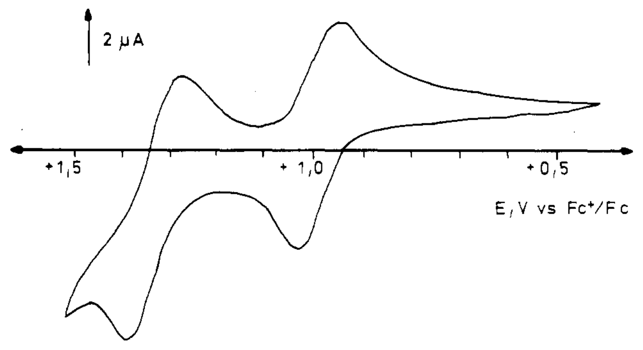


Figure 1. Cyclic voltammogram of $[FeL_2][FeLL^1](ClO_4)_4$ in acetonitrile (0.1 M $[n\text{-}Bu_4N]PF_6$ supporting electrolyte, Pt-button working electrode, 20 °C).

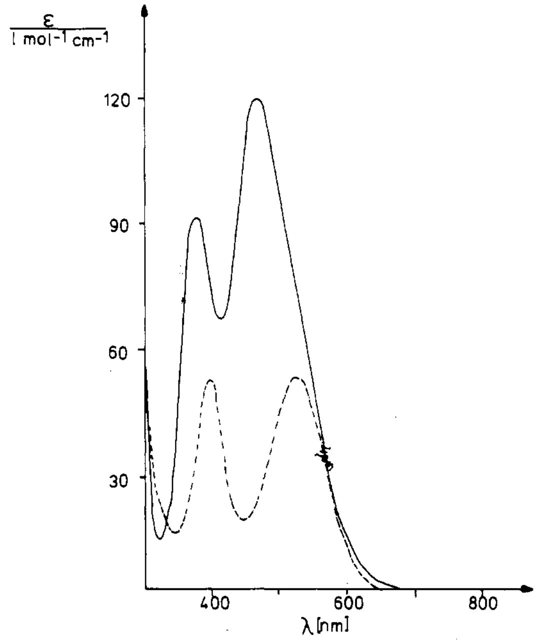


Figure 2. Electronic spectra of $[FeL_2](ClO_4)_2$ (---) and of $[FeLL^1](ClO_4)_2 \cdot 2NaClO_4 \cdot H_2O$ (—) measured in H_2O (20 °C).

Magnetic Properties and Electronic Spectra. The electronic ground state of iron(III) in a strong octahedral ligand field is $^2T_{2g}$. The temperature dependence of the magnetic moment of this paramagnetic ion depends on the energy distortion of the $^2T_{2g}$ term and on the effective spin–orbit coupling parameter.[27] The magnetic moment is expected to be above the spin-only value (1.73 μ_B) and less than about 2.5 μ_B. For $[FeL_2](PF_6)_3$ the effective magnetic moment increases from 2.09 μ_B at 110 K to 2.46 μ_B at 293 K. These values are very similar to those of $K_3[Fe(CN)_6]$[28] and indicate a genuine low-spin iron(III) center in a pseudooctahedral ligand field of six thioether sulfur donor atoms.

$[Fe^{II}LL^1](ClO_4)_2 \cdot 2NaClO_4 \cdot H_2O$ was found to be diamagnetic in the solid state and in solution, as is $[Fe^{II}L_2](ClO_4)_2$.[17] Thus

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[26] Nonoyama, M.; Nonoyama, K. *Transition Met. Chem. (Weinheim, Ger.)* **1985**, *10*, 382.

[27] Figgis, B. N.; Lewis, J. *Prog. Inorg. Chem.* **1964**, *6*, 37–239.

[28] Figgis, B. N. *Trans. Faraday Soc.* **1961**, *57*, 204 and references therein.

Table IV. Spectroscopic Data and Magnetic Properties of Complexes (L = 1,4,7-Trithiacyclononane, L′ = 1,4,7-Trithiacyclononane 1-Oxide)

complex	color	electronic spectrum λ_{max}, nm (ϵ, L mol^{-1} cm^{-1})	μ_{eff}, μ_B	ref
$[Fe^{II}L_2](ClO_4)_2$	purple	523 (53), 395 (52)	diamag	17
$[FeLL^1](ClO_4)_2\cdot 2NaClO_4\cdot H_2O$	orange-brown	465 (123), 374 (96), 268 (1.6×10^4)^a	diamag	this work
$[FeL_2](PF_6)_3$	green	634 (700), 587 (sh), 498 (sh), 458 (520), 340 (7600)^b	2.09 (110 K), 2.46 (293 K)	this work

^{a}Measured in H_2O. ^{b}Measured in CH_3CN.

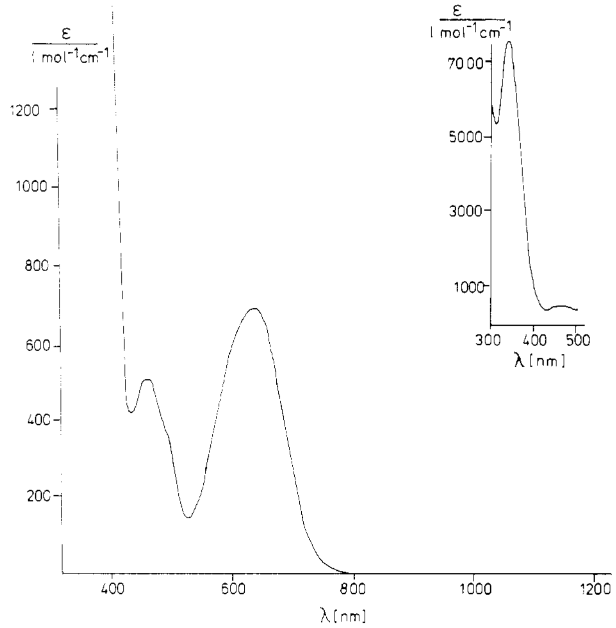

Figure 3. Electronic spectrum of $[FeL_2](PF_6)_3$ in CH_3CN (20 °C).

the iron centers in these thioether complexes are in the ferrous low-spin state.

Figure 2 shows the electronic spectra of $[FeL_2]^{2+}$ and $[FeLL^1]^{2+}$, which each exhibit two d–d absorption maxima typical of low-spin iron(II) (d^6) that are not obscured by intense charge-transfer bands of the metal-to-ligand type as is often the case in Fe(II) complexes with aromatic or unsaturated nitrogen-donor ligands.[29] From the $[FeL_2]^{2+}$ spectrum the ligand field parameter Dq has been calculated previously[17] to be 2067 cm^{-1} and the Racah parameter B = 387 cm^{-1}. For the analogous hexaaza complex $[Fe([9]aneN_3)_2]^{2+}$, Dq has been determined to be 1894 cm^{-1} and B = 575 cm^{-1}. These values indicate that 1,4,7-trithiacyclononane exerts a very strong ligand field, contrary to the common belief that thioether ligands are weak ligands.[39]

The two d–d transitions, ${}^1A_{1g} \rightarrow {}^1T_{1g}$ and ${}^1A_{1g} \rightarrow {}^1T_{2g}$, in $[FeLL^1]^{2+}$ are shifted to shorter wavelengths as compared to those in $[FeL_2]^{2+}$, and interestingly, the molar extinction coefficients are substantially larger (Table IV, Figure 2). This is a clear indication that the Laporte-forbidden transitions in centrosymmetric $[FeL_2]^{2+}$ (the FeS_6 core has O_h symmetry[17]) are allowed in $[FeLL^1]^{2+}$, which is noncentrosymmetric due to the presence of one S-coordinated sulfoxide.

Figure 3 shows the electronic spectrum of $[FeL_2]^{3+}$. Low-spin d^5 has a ground state of ${}^2T_{2g}$ in O_h arising from $t_{2g}{}^5$. Low-spin Fe(III) in O_h is quite uncommon. The most carefully studied example appears to be $[Fe(CN)_6]^{3-}$, the electronic spectrum of which is dominated by charge-transfer bands, but four weak features in a crystal of KCl doped with $[Fe(CN)_6]^{3-}$ have been assigned as d–d transitions to doublet and quartet states.[30] The electronic spectrum of $[FeL_2]^{3+}$ is quite unique in the respect that four bands of considerable intensity are observed in the visible region, which may be assigned to d–d transitions, and a very intense band is seen at 340 nm, which is probably a metal-to-ligand charge-transfer band. The $t_{2g}{}^4e_g{}^1$ configuration gives rise to ${}^4T_{1g}$, ${}^4T_{2g}$, ${}^2A_{1g}$, 2 ${}^2E_g$, 2 ${}^2T_{1g}$, and 2 ${}^2T_{2g}$, and in analogy to the case for $[Fe(CN)_6]^{3-}$ the four d–d transitions of $[FeL_2]^{3+}$ may be tentatively assigned as follows: 634 (${}^1T_{1g}$), 587 (${}^4T_{2g}$), 498 (${}^2A_{2g}$, ${}^2T_{1g}$), and 458 nm (${}^2E_g$). On the other hand, the Mössbauer spectrum of $[FeL_2]^{3+}$ quite convincingly shows that the symmetry of the $[FeS_6]^{3+}$ core cannot be regular octahedral (O_h) but probably is D_{4h} (elongated octahedron) even at room temperature (see below).

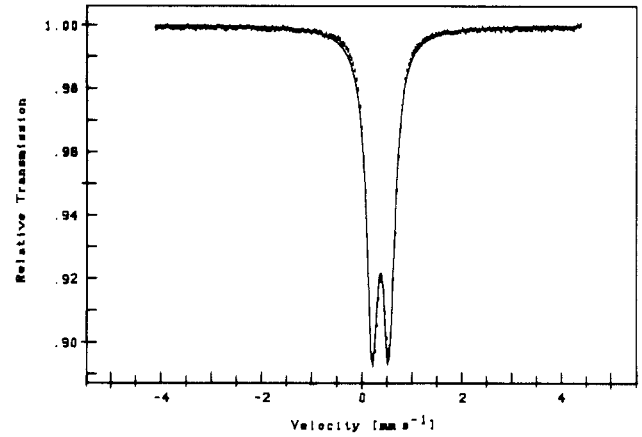

Figure 4. Mössbauer spectrum of $[FeL_2](ClO_4)_2$ at 4.2 K. The solid line is a least-squares fit using Lorentzian lines.

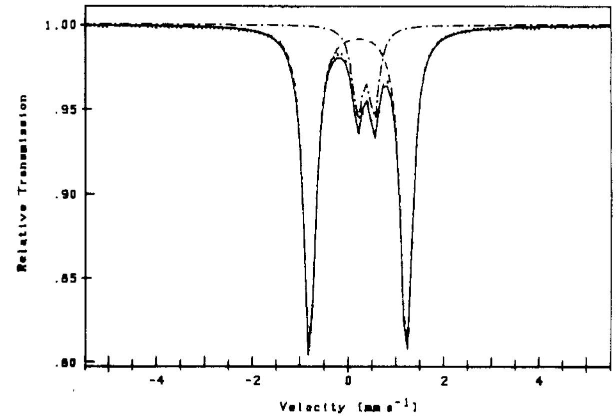

Figure 5. Mössbauer spectrum of $[FeL_2](PF_6)_3$ at 4.2 K. The sample contained 20% $[FeL_2]^{2+}$ impurity. Solid and dashed lines are least-squares fits using Lorentzian lines.

Mössbauer Study of $[FeL_2]^{2+}$ and $[FeL_2]^{3+}$. The measured spectra and fitted quadrupole doublets are shown in Figure 4 for $[FeL_2](ClO_4)_2$ and in Figure 5 for $[FeL_2](PF_6)_3$. The sample of $[FeL_2](PF_6)_3$ was stored under an argon atmosphere at ambient temperature for 6 days after its preparation before the spectrum was recorded. Consequently, the sample contained 18% of $[FeL_2]^{2+}$, which increased to ~28% after further 2 weeks of storage.

Both the isomer shift (δ relative to α-Fe at room temperature) and quadrupole splitting (ΔE_Q) of $[Fe^{II}L_2]^{2+}$ (Table V) are typical

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(29) Lever, A. B. P. *Inorganic Electronic Spectroscopy*; Elsevier: Amsterdam, 1984.

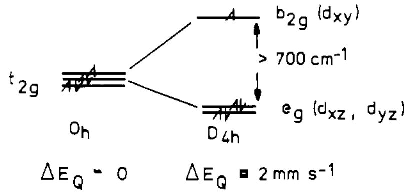
(30) (a) Alexander, J. J.; Gray, H. B. *J. Am. Chem. Soc.* **1968**, *90*, 4260. (b) Gale, R.; McCaffery, A. J. *J. Chem. Soc., Dalton Trans.* **1973**, 1344.

Table V. Isomer Shifts (δ) and Quadrupole Splittings (ΔE_Q) of $[FeL_2](ClO_4)_2$ and $[FeL_2](PF_6)_3$ at Various Temperatures

complex	temp, K	δ, mm s^{-1} [a,b]	ΔE_Q, mm s^{-1} [a]
$[Fe^{II}L_2]^{2+}$	4.2	0.35	0.33
	77	0.34	0.33
	293	0.27	0.32
$[Fe^{III}L_2]^{3+}$	4.2	0.20	2.02
	293	0.11	1.91
$[Fe^{III}([9]aneN_3)_2]^{3+}$	298	−0.02	0.98

[a] Standard error: ±0.01 mm s^{-1}. [b] Relative to α-Fe at room temperature.

Scheme I



of the ferrous low-spin state of a hexacoordinated iron.[31] They compare well for example with corresponding values derived from a 4.2 K measurement of CO-myoglobin ($\delta = 0.266$ mm s^{-1} and $\Delta E_Q = 0.363$ mm s^{-1}), the heme iron of which is known to be in the ferrous low-spin state and is hexacoordinated.[32]

Removal of an electron from t_{2g}^6 of $[FeL_2]^{2+}$ yields t_{2g}^5 for $[FeL_2]^{3+}$. If the point symmetry of the iron(III) center is close to O_h symmetry (regular FeS_6 octahedron), an equal distribution of the five electrons among the t_{2g} orbitals is expected—at least at room temperature—and, consequently, the quadrupole splitting would be close to zero at 300 K.[31] This has been observed for $[Fe(CN)_6]^{3-}$,[33] where the quadrupole splitting takes the value $\Delta E_Q = 0.5$ mm s^{-1} at 4.2 K and decreases with increasing temperature. Clearly, this is not the case for $[FeL_2]^{3+}$ (Figure 5, Table V). Instead, the quadrupole splitting of $[FeL_2]^{3+}$ is relatively large ($\Delta E_Q = 2.02$ mm s^{-1}) and is scarcely temperature dependent between 4.2 and 300 K. Therefore, we conclude that the deviation from cubic point symmetry of the iron(III) center in the FeS_6 core is quite considerable. t_{2g}^5 in O_h symmetry is Jahn–Teller unstable; the orbital degeneracy would be lifted by a static distortion of the FeS_6 core along the z axis ($O_h \rightarrow D_{4h}$), resulting in an elongated FeS_6 octahedron. The energy spacing between e_g and b_{2g} must be $\geqslant 700$ cm^{-1} (Scheme I) in order to be consistent with the observed nearly temperature independent quadrupole splitting.

Thus, $[FeL_2]^{3+}$ represents the rare case of an static Jahn–Teller-distorted t_{2g}^5 metal ion complex at room temperature. The thioether sulfur donors are quite strong σ donors and have π-acceptor properties, which make the t_{2g} orbitals bonding rather than nonbonding in complexes with pure σ-donor ligands, and consequently, a static Jahn–Teller effect may be observed even at room temperature.

It is of interest to compare these results with those for the analogous bis(1,4,7-triazacyclononane)iron(III) complex, which has been shown to be also low spin[34] and which has been characterized by X-ray crystallography.[35] An isomer shift of −0.02 (2) mm s^{-1} and a quadrupole splitting of only 1.0 mm s^{-1} at 295 K have been observed for $[Fe([9]aneN_3)_2]Cl_3{\cdot}5H_2O$, which is in excellent agreement with the crystallographic determination at 298 K showing six equivalent (within experimental error) Fe(III)–N bonds (1.99 (1) Å; dynamic Jahn–Teller effect). An X-ray structure determination of an $[FeL_2]^{3+}$-containing salt would be of great interest, but the lack of suitable single crystals and the slow decomposition of $[FeL_2]^{3+}$—even in the solid state—have hampered these studies to date.

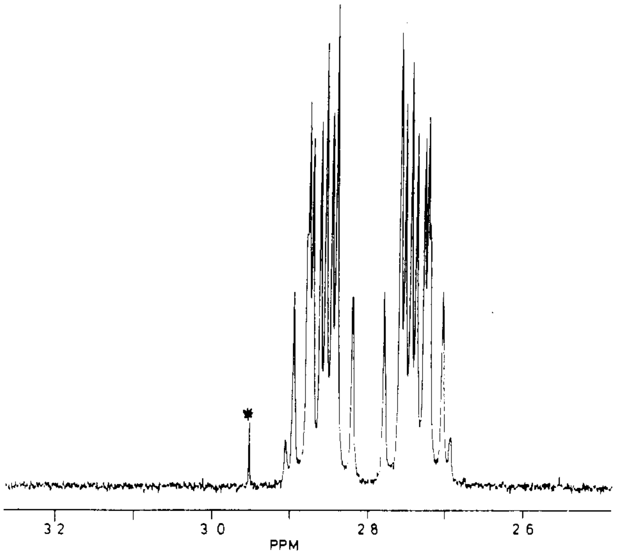


Figure 6. ^1H NMR spectrum (400 MHz) of $[FeL_2](ClO_4)_2$ in D_2O (the asterisk marks an impurity).

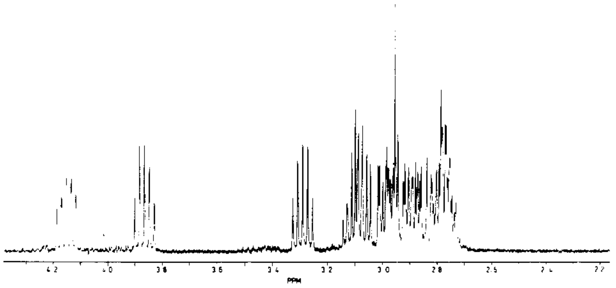


Figure 7. ^1H NMR spectrum (400 MHz) of $[FeLL_1](ClO_4)_2{\cdot}2NaClO_4{\cdot}H_2O$ in D_2O (the asterisk marks an impurity).

Finally, it is noted that the observed increase of the isomer shift at 4.2 K of 0.15 mm s^{-1} as one goes from $[FeL_2]^{3+}$ to $[FeL_2]^{2+}$ is in good qualitative agreement with the ferric low-spin and the ferrous low-spin ground state of the respective iron centers in the two complexes. Removal of an electron from the Fe 3d shell deshields the nuclear potential and increases the electron density of the iron nucleus and thus decreases δ.[31] Mössbauer spectroscopy in addition to magnetic susceptibility measurements clearly indicates that the oxidation of $[FeL_2]^{2+}$ to $[FeL_2]^{3+}$ by PbO_2 is metal-centered.

^1H NMR Spectra. Figure 6 shows the ^1H NMR spectrum in D_2O of $[FeL_2]^{2+}$, which displays two symmetrical groups of signals of the methylene protons (δ_1 2.90–2.81 and δ_2 2.78–2.69). These signals correspond to 12 protons in equatorial positions and 12 protons in axial positions with respect to the two planes of the coordinated 1,4,7-trithiacyclononane. These two groups of protons are magnetically nonequivalent because they are oriented differently toward the Fe(II) center, which leads to a small difference of the respective chemical shifts of 0.21 ppm. The ^{13}C NMR spectrum displays one signal for the methylene carbon atoms (δ 36.58).

The ^1H NMR spectrum of $[FeLL^1](ClO_4)_2{\cdot}2NaClO_4{\cdot}H_2O$ in D_2O is shown in Figure 7. It is considerably more complicated than that of $[FeL_2]^{2+}$. Three pseudoquintets (δ_1 4.12–4.19, δ_2 3.83–3.90, δ_3 3.25–3.32) and a complex multiline signal (δ 2.73–3.14) are observed. Each of the first three signals corresponds to two methylene protons and the last to 18 H. The ^{13}C NMR spectrum exhibits five signals (δ 61.45, 37.52, 37.38, 37.05, 36.45).

A COSY experiment revealed that the three multiplets in the ^1H NMR spectrum, each of which corresponds to two protons, couple among each other and, in addition, with one multiplet

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(31) Gütlich, P.; Link, R.; Trautwein, A. X. In *Mössbauer Spectroscopy in Transition Metal Chemistry*; Springer-Verlag: Heidelberg, 1978.

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(34) Wieghardt, K.; Schmidt, W.; Herrmann, W.; Küppers, H. J. *Inorg. Chem.* **1983**, *22*, 2953–2956.

(35) Boeyens, J. C. A.; Forbes, A. G. S.; Hancock, R. D.; Wieghardt, K. *Inorg. Chem.* **1985**, *24*, 2926–2931.

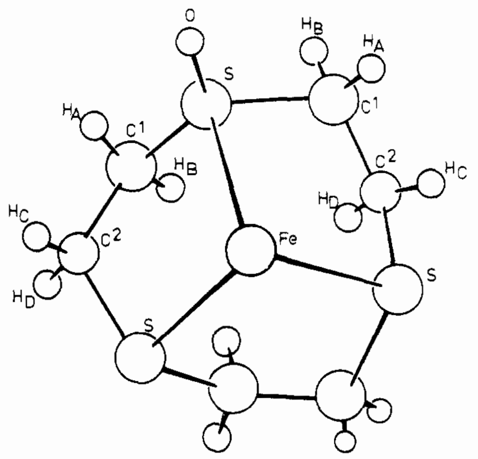

Figure 8. Atom-labeling scheme for coordinated 1,4,7-trithiacyclononane 1-oxide.

centered around δ 2.8. Therefore, we suggest that these four groups of signals are due to the ethylene groups of one coordinated 1,4,7-trithiacyclononane 1-oxide.

In the following we attempt a further assignment of the ^{1}H NMR signals. For this purpose we have labeled the carbon atoms and methylene protons as shown in Figure 8. Because of the relatively large chemical shift of the multiplet at 4.12–4.19 ppm, we assign this signal to the protons H_A that are bound equatorially to C^1. The electric field effect of the neighboring S=O bond causes a polarization of the C^1–H bond electrons and, as a consequence of this, a deshielding of the two H_A protons. This behavior has been described previously for some cyclohexyl phenyl sulfoxides. The COSY experiment indicates a geminal coupling of H_A to the protons of the second multiplet at 3.83–3.90 ppm, which we therefore assign to H_B protons; a vicinal coupling of H_A with protons of the multiplets at 3.25–3.32 and 2.73–3.14 ppm is also observed, which we assign according to the diminishing electric field effect of the S=O group to protons H_C and H_D, respectively. The multiline signal at 2.73–3.14 (18 H) is then due to 12 methylene protons of the coordinated 1,4,7-trithiacyclononane and the ethylene group opposite the S=O group in 1,4,7-trithiacyclononane 1-oxide (4 H) and two H_D protons. A more detailed interpretation is at present not possible. The carbon atom exhibiting the most positive chemical shift at 61.45 ppm is assigned to C^1, the two carbon atoms attached to the S=O group, in excellent agreement with previously reported values for such α-carbon atoms in sulfoxides.[36] The other carbon atoms are all bonded to thioether sulfur atoms and are much more shielded (37.5–36.45 ppm).

The ^{1}H NMR spectrum of the mixed crystals, obtained at the beginning of the precipitation after addition of $NaClO_4$ to the reaction mixture, is quite similar to that shown in Figure 7. Only the intensity and number of the signals of the multiplet at 2.95–2.7 ppm increase due to the presence of unreacted $[FeL_2]^{2+}$. The spectrum is a superposition of the spectra shown in Figures 6 and 7. The intensity of the signals at 4.12–4.19, 3.83–3.90, and 3.25–3.32 ppm, each of which corresponds to two protons of one coordinated 1,4,7-thiacyclononane 1-oxide, may be used to determine the ratio of $[FeLL^1]^{2+}$:$[FeL_2]^{2+}$, which was found to be 1:1. Thus, the orange mixed crystals consist of $[FeLL^1](ClO_4)_2[FeL_2](ClO_4)_2$ in agreement with an X-ray diffraction study (see below).

Description of the Structure of $[FeLL^1](ClO_4)_2 \cdot 2NaClO_4 \cdot H_2O$. Table III gives bond distances and angles of the two independent cations $[FeLL^1]^{2+}$ in the triclinic unit cell; the corresponding values are within experimental error identical for the two cations. Figure 9 is a perspective view of cation II. As has been shown conclusively from the ^{1}H NMR measurements, each iron(II) center is coordinated to one 1,4,7-trithiacyclononane and one 1,4,7-trithiacyclononane 1-oxide ligand. These $[FeLL^1]^{2+}$ cations are disordered in the crystals since the Fe atoms are located on crystallographic centers of symmetry at (0, 0, 0) and ($^1/_2$, $^1/_2$, $^1/_2$). In agreement with this composition the occupancy factors of the sulfoxide oxygen atoms O1 and O2 when treated as variables were refined smoothly to values of 0.47 and 0.49, respectively, and were set to 0.5 in the last refinement cycle. In addition, the anisotropic temperature factors of O1 and O2 adopted much more reasonable values when the occupancy factors were 0.5 rather than 1.0, and the final discrepancy factors R and R_w are slightly smaller for this model.

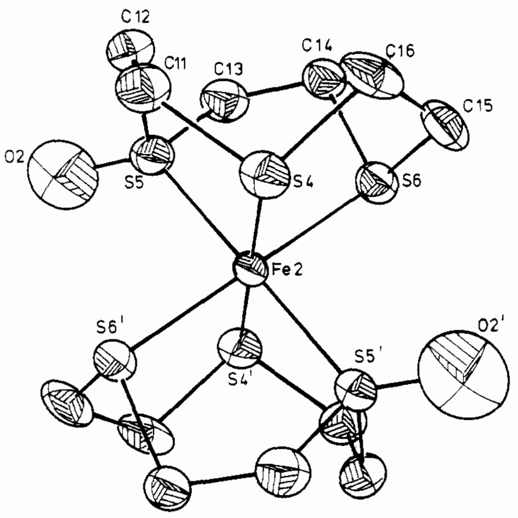

Figure 9. Perspective view of one of the disordered cations $[FeLL^1]^{2+}$ in $[FeLL^1](ClO_4)_2 \cdot 2NaClO_4 \cdot H_2O$. Note that O2 and O2′ possess half the site occupancy of carbon and sulfur atoms. Thermal ellipsoids enclose 40% probabilities.

The Fe–S thioether bond distances (average 2.258 (1) Å) in $[FeLL^1]^{2+}$ compare well with those found in $[FeL_2](PF_6)_2$[17] (average 2.246 (1) Å), whereas the Fe–S sulfoxide bond distance exhibits some shortening (2.207 Å), the exact bond distance of which is not known due to the disorder. The true Fe–S(O) bond length may be estimated to be 2.16 Å if one assumes that the measured Fe–S(O) distance of 2.207 Å is the arithmetic mean of the true Fe–S(O) distance and a thioether Fe–S bond length of 2.255 Å. The S–Fe–S bond angles in $[FeLL^1]^{2+}$ do not deviate significantly from 90°.

The average S–O bond distance of 1.498 (7) Å is in good agreement with other S-coordinated sulfoxides;[37] C–S and C–C bond distances are normal.

The arrangement of the four sodium cations, perchlorate anions, and molecules of water of crystallization in the unit cell is quite interesting. They form two independent strands: Na1 is surrounded in a distorted-octahedral fashion by six oxygen atoms (O11 and O13 of one ClO_4^-, O21, O22, and O24 of a second ClO_4^-, and the molecule of water of crystallization); the Na–O bond distances are in the usual range (2.331 (6)–2.674 (4) Å). The first ClO_4^- is coordinated in a bidentate fashion to Na1 whereas the second ClO_4^- is coordinated in a bidentate fashion to this sodium cation but is also bridging to Na1′. This strand is not connected via Na⋯O bonds or hydrogen bonding of the water molecule to the sulfoxide groups with the cations, and consequently, there is no disorder observed.

In contrast, the second sodium cation is coordinated to the sulfoxide oxygen atoms, and the two locations Na2 and Na3, each with an occupancy of 0.5, were determined (O1–Na3 = 2.575 (9) Å and O2–Na2 = 2.417 (7) Å). The two positions are quite close to each other (Na2⋯Na3 = 0.836 (7) Å), and the four oxygen atoms of $(Cl(4)O_4^-$ are flipping between two distinct positions, which have been refined smoothly with anisotropic thermal parameters (eight O atoms with an occupancy factor 0.5; O41–48). Na2 is distorted octahedrally surrounded by six oxygens (Na2–O distances range between 2.283 (6) and 2.555 (6) Å) as is Na3

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(Na3–O distances 2.216 (10)–2.862 (8) Å). (Cl3)O_4^- is not disordered.

Finally, we have also solved the structure of a mixed crystal of $[FeL_2][FeLL^1](ClO_4)_4$.[38] There are two formula units in the triclinic space group $P\bar{1}$; the iron(II) centers are located on two crystallographic centers of symmetry at (0, 0, 0) and (0, $^1/_2$, $^1/_2$), with a occupancy factors of 0.5. Thus, the $[FeL_2]^{2+}$ and $[FeLL^1]^{2+}$ cations are again statistically disordered. When the occupancy factors of the two independent sulfoxyl oxygen atoms were treated as variables in the last refinement cycles, these values converged at 0.20 and 0.33 (mean 0.265), indicating that the distribution of the two cations in the unit cell may not be completely at random, but the structure determination does confirm within experimental error the ratio of $[FeL_2]^{2+}/[FeLL^1]^{2+}$ to be 1:1 as was determined from ^1H NMR measurements. The gross overall structure of the cations is identical with the one shown in Figure 9 with the exception of the apparent Fe–S(O) bond distance of the iron–sulfoxide bond, which is longer (average 2.224 (1) Å) than the one observed in $[FeLL^1](ClO_4)_2 \cdot 2NaClO_4 \cdot H_2O$ due to the superimposed thioether Fe–S bonds of $[FeL_2]^{2+}$ and of $[FeLL^1]^{2+}$. If this is taken into account, a true Fe–S(O) bond distance of 2.16 Å may be calculated, in excellent agreement with the previous estimate (see above). The ClO_4^- anions were not found to be disordered; their oxygen atoms were readily refined with reasonable anisotropic thermal parameters.

Conclusion. We have shown in this study that the crown thioether 1,4,7-trithiacyclononane forms stable complexes of iron(II/III). Oxidation of $[FeL_2]^{2+}$ with PbO_2 leads to the homoleptic low-spin $[Fe^{III}L_2]^{3+}$ cation, which is a very strong one-electron oxidant. Magnetic susceptibility and Mössbauer measurements unambiguously show that the oxidation is metal-centered and that the low-spin $[FeS_6]^{3+}$ core is Jahn–Teller-distorted even at room temperature. This shows that saturated crown thioether ligands coordinate also to metal centers in high oxidation states, although the lower oxidation states are clearly stabilized by the thioether π-acceptor properties, contrasting in this respect with the case for the pure σ-donor 1,4,7-triazacyclononane.[39]

Depending on the nature of the oxidant used, it is also possible to oxidize the coordinated thioether ligand in $[FeL_2]^{2+}$ without concomitant oxidation of the metal center. Thus, sodium peroxodisulfate was found to yield $[FeLL^1]^{2+}$ cations, which contain one coordinated 1,4,7-trithiacyclononane 1-oxide in addition to one 1,4,7-trithiacyclononane ligand.

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Supplementary Material Available: Tables S1, S2, S2A, and S2B for $[FeLL^1](ClO_4)_2 \cdot 2NaClO_4 \cdot H_2O$, listing calculated positional parameters of hydrogen atoms, thermal parameters, bond distances, and bond angles, Tables S4–10 for $[FeL_2][FeLL^1](ClO_4)_4$, listing experimental details of the structure determination, atomic coordinates, bond lengths and bond angles, thermal parameters, and calculated coordinates of hydrogen atoms, and perspective views of the iron coordination environments in $[FeL_2][FeLL^1](ClO_4)_2$ (12 pages); Tables S3 and S10, listing calculated and observed structure factors for both compounds (55 pages). Ordering information is given on any current masthead page.

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(38) Crystal data for $[FeL_2][FeLL^1](ClO_4)_4$: $C_{24}H_{48}Cl_4Fe_2O_{17}S_{12}$; mol wt 1249.2; triclinic; space group $P\bar{1}$; $a = 8.848$ (8), $b = 11.499$ (6), $c = 11.679$ (7) Å; $\alpha = 86.04$ (5), $\beta = 84.48$ (8), $\gamma = 72.40$ (5)°; $V = 1126.2$ (7) Å^3, $Z = 2$; $d_{calcd} = 1.84$ g cm^{-3}; $\mu = 14.9$ cm^{-1}; crystal dimensions 0.26 × 0.26 × 0.35 mm^3; 6620 measured reflections ($3.0 < 2\theta < 60°$) and 3023 unique reflections ($I \geqslant 2\sigma(I)$); radiation Mo Kα; empirical absorption correction; 275 least-squares parameters; anisotropic thermal parameters for all non-hydrogen atoms; H atoms in calculated positions (d(C–H) = 0.96 Å sp^3-hybridized carbon atoms) with common isotropic $U = 0.058$ Å^2; $R = 0.033$; $R_w = 0.032$; GOF = 2.0; shift/esd in last cycle 0.01 (mean), 0.06 (maximum). Tables of atom coordinates, anisotropic temperature factors, bond distances and angles, and observed and calculated structure amplitudes are available as supplementary material.

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Crown Thioether Chemistry. Ruthenium(II) Complexes of 1,4,7-Trithiacyclononane and 1,5,9-Trithiacyclododecane

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Reaction of $[Ru(Me_2SO)_6](BF_4)_2$ with tridentate thioether ligands in methanol yields the oxidatively and hydrolytically robust complexes $[RuL_2]^{2+}$ (L = 2,5,8-trithianonane, 1,4,7-trithiacyclononane (9S3), and 1,5,9-trithiacyclododecane (12S3)), in which the central Ru(II) ion coordinates to an octahedral array of six thioether S atoms. Optical, NMR, electrochemical, and single-crystal X-ray diffraction studies of the latter two complexes provide a benchmark for the development of the coordination chemistry of thioethers with heavy transition elements in moderate and low oxidation states. Crystal data for $[Ru(9S3)_2](CF_3SO_3)_2$: $a = 7.677$ (5) Å, $b = 9.465$ (3) Å, $c = 18.423$ (3) Å, $\alpha = 83.61$ (2)°, $\beta = 88.48$ (4)°, $\gamma = 83.05$ (4)°; triclinic, space group $P\bar{1}$; final $R = 4.03\%$, $R_w = 4.82\%$. Crystal data for $[Ru(12S3)_2](BF_4)_2 \cdot 2MeNO_2$: $a = 20.355$ (3) Å, $b = 8.006$ (3) Å, $c = 22.540$ (2) Å, $\beta = 114.844$ (9)°; monoclinic, space group $I2/a$; final $R = 2.85\%$, $R_w = 3.32\%$.

Introduction

Complexes of simple mono- and bidentate thioethers with heavy transition-metal ions have long attracted interest because of their potential analogy to catalytically active phosphine complexes.[1-3] In a broader context this possible parallel raises the issue of the electronic consequences of thioether coordination, a question that has also risen recently with regard to the blue copper proteins.[4] This question is most simply and rigorously addressed in complexes that only have thioether ligands. Unfortunately, however, to date few such homoleptic thioether complexes have proven synthetically tractable owing to the low stability of ML_6 (L = Me_2S) and $M(L\text{-}L)_3$ (L-L = $MeSCH_2CH_2SMe$) complexes.[5]

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