Iron(II)–α-Amino Acid Complexes from Nonprotic Solutions: Reactions of [Fe(Mes)$_2$(phen)] with α-Amino Acids and the Structures of Bis(L-Prolinato)(1,10-phenanthroline)iron(II) and Bis(D-prolinato)(1,10-phenanthroline)iron(II)

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The arylation of FeCl$_2$(THF)$_{1.5}$ in THF with MesMgBr (Mes = 1,3,5-Me$_3$C$_6$H$_2$) in the presence of 9,10-phenanthroline (phen) led to the crystalline [Fe(phen)(Mes)$_2$], **1**, which contains a tetrahedral iron(II) σ-bonded to two aryl groups. They can be removed by a variety of protic ligands under aprotic conditions. The reaction of **1** with amino acids AH led to the isolation of monomeric iron(II)–amino acid complexes [Fe(phen)(A)$_2$] [A = L-prolinato (**2**), D-prolinato (**3**), L-phenylalaninato (**4**), D-phenylalaninato (**5**), DL-phenylalaninato (**6**), L-tryptophanato (**7**), L-valinato (**8**)]. They show a diversity in solubility depending on the amino acid residue. All of them have been fully characterized including the X-ray analysis on **2** and **3**, which have been shown to be enantiomeric forms. Crystallographic details: **1** is monoclinic, space group *I*2/*a*, with a = 13.216(3) Å, b = 14.843(3) Å, c = 15.904(3) Å, $\alpha = \gamma = 90°$, β = 102.32(2)°, Z = 4, and R = 0.044. **2** is hexagonal, space group $P3_121$, with $a = b$ = 9.663(2) Å, c = 23.743(4) Å, $\alpha = \beta = 90°$, $\gamma = 120°$, Z = 3, and R = 0.035. **3** is hexagonal, space group $P3_221$, with $a = b$ = 9.692(1) Å, c = 23.841(3) Å, $\alpha = \beta = 90°$, $\gamma = 120°$, Z = 3, and R = 0.053.

Introduction

Iron is the most abundant and chemically versatile transition metal[1] used by nature, and it is essential for virtually all forms of life. The element is implicated in many important biological processes including oxygen uptake and transport, nitrogen fixation, DNA synthesis, and electron transport in photosynthesis. Accordingly, the biochemistry of iron has been extensively studied and has been the subject of several reviews.[2] Little is known, however, about the ways in which iron coordinates to α-amino acids, especially in nonaqueous media. Some rare spectroscopic information is available on binding of amino acids in aqueous solutions by iron(II),[3] and there are rare structural data on iron(III) polynuclear[4a] and iron(II) mononuclear systems.[4b]

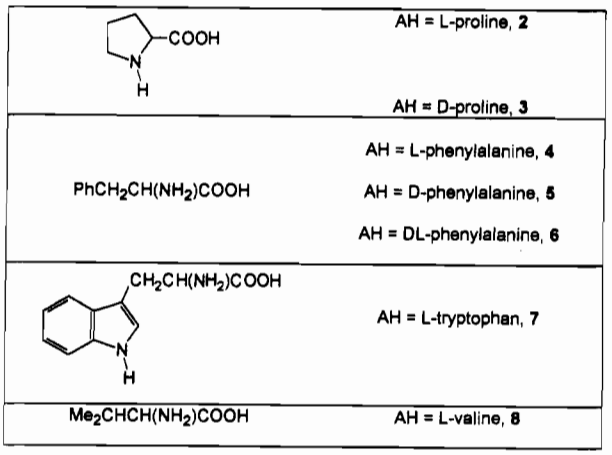
We have recently developed a new approach to metal–amino acid chemistry, involving the synthesis of amino acid complexes in nonprotic solutions. This has allowed us to prepare a number of novel complexes. In our first paper, we described some vanadium(III)–α-amino acid complexes.[5] We now report the preparation in THF solution of a series of bis(amino acidato)iron(II) complexes and describe the crystal structures of two of these, bis(L-prolinato)(1,10-phenanthroline)iron(II) and bis(D-prolinato)(1,10-phenanthroline)iron(II).

Results and Discussion

Dimesityliron(II) 1,10-phenanthroline, [Fe(Mes)$_2$(phen)], **1** [Mes = 2,4,6-MeC$_6$H$_2$], was chosen as the starting material for this work since it is easily prepared, and readily reacts with protic sources such as α-amino acids, AH, to form [Fe^{II}(A)$_2$(phen)] complexes by liberating mesitylene (eq 1).

$$[Fe(Mes)_2(phen)] + 2\,AH \longrightarrow [Fe(A)_2(phen)] + 2\,MesH \qquad (1)$$

1 **2-8**



[Fe(Mes)$_2$(phen)], **1**, was prepared in a manner similar to that for [Fe(Mes)$_2$]$_2$,[6] by the reaction of FeCl$_2$·1.5THF with 2 equiv of MesMgBr, followed by the addition of 1,10-phenanthroline. After workup, violet [Fe(Mes)$_2$(phen)] was isolated in 66% yield. The structure of **1** is shown in Figure 1. The tetrahedral complex is monomeric in contrast to the dimeric structure of [Fe$_2$(Mes)$_4$].[7] The structure of complex **1** consists of discrete mononuclear [Fe(Mes)$_2$(phen)] units and Et$_2$O solvent molecules in the molar

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Table 1. Experimental Data for the X-ray Diffraction Studies on Crystalline Compounds 1–3

	compound		
	1	**2**	**3**
formula	$C_{30}H_{30}FeN_2 \cdot C_4H_{10}O$ (1/1)	$C_{22}H_{24}FeN_2O_4 \cdot C_2H_6OS$ (1/1)	$C_{22}H_{24}FeN_2O_4 \cdot C_2H_6OS$ (1/1)
a, Å	13.216(3)	9.663(2)	9.692(1)
b, Å	14.843(3)	9.663(2)	9.692(1)
c, Å	15.904(3)	23.743(4)	23.841(3)
α, deg	90.00	90	90
β, deg	102.32(2)	90	90
γ, deg	90	120	120
V, Å^3	3048.0(11)	1920.0(7)	1939.5(4)
Z	4	3	3
fw	538.5	514.4	514.4
space group	$I2/a$ (No. 15)	$P3_121$ (No. 152)	$P3_221$ (No. 154)
t, °C	22	22	22
λ, Å	0.710 69	0.710 69	0.710 69
ρ_{calc}, g cm^{-3}	1.173	1.335	1.321
μ, cm^{-1}	5.21	7.06	6.99
transm coeff	0.914–1.000	0.943–1.000	0.907–1.000
no. of unique tot. data	2126	2796	2814
no. of unique obsd data	944	1243	1331
R^a	0.044	0.035	0.053
$R_G{}^b$	0.100	0.073	0.150
GOF^c	0.71	0.56	0.88

^{a} $R = \Sigma|\Delta F|/\Sigma|F_o$ for unique observed data [$I > 2\sigma(I)$]. ^{b} $R_G = [\Sigma w|\Delta F|^2/\Sigma w|F_o|^2]^{1/2}$. ^{c} GOF = $[\Sigma(w\Delta F^2)^2/(NO-NV)]^{1/2}$.

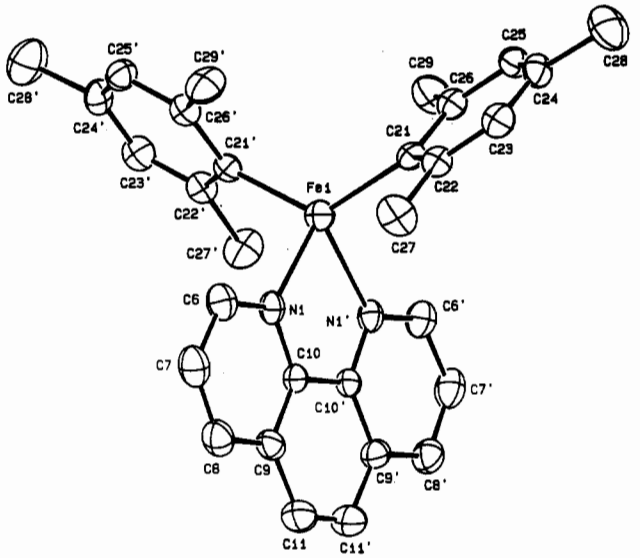

Figure 1. ORTEP drawing for complex **1** (30% probability ellipsoids).

ratio 1/1 separated by van der Waals contacts. The iron atom is tetrahedrally surrounded by two σ-bonded mesityl ligands and the nitrogen atoms of the chelating *o*-phenanthroline molecule (Figure 1). In Table 5 are quoted selected bond distances and angles. The complex molecule possesses a crystallographically imposed C_2 symmetry, the 2-fold axis running through the metal atom and the middle points of the C10–C10′ and C11–C11′ bonds (′ = 0.5 − x, y, −z) of the phen molecule. The Fe–C bond distance [2.063(4) Å] is in good agreement with the values observed for [$Fe_2(Mes)_4$] [Fe–$C_{terminal}$ = 2.023(5) Å (average)].[7] The iron atom is displaced by the mesityl ring plane by only 0.031(1) Å. The Fe–N [2.155(4) Å] bond distance falls in the range of values observed for Fe–N bond distances in other mono(phenanthroline)-iron(II) complexes.[8] The phenanthroline ligand is planar within experimental error, and the iron atom lies exactly on that plane. The mesityl ligands are nearly perpendicular to the phen molecule [dihedral angle 75.7(1)°]. They adopt an orientation permitting four hydrogen atoms from four *o*-methyl carbons to approach the iron atom at distances of 2.56 and 2.78 Å for H291 and H271, respectively, in an approximate tetrahedral arrangement.

Reaction 1 proceeded smoothly and was limited only by the choice of amino acid since only a few of the proteinogenic α-amino acids have some discernible solubility in aprotic organic solvents.

Table 2. Fractional Atomic Coordinates (×10^4) for Complex 1

atom	x/a	y/b	z/c
Fe1	2500	1673.9(7)	0
O1	7500	4312(4)	0
N1	1760(3)	530(3)	448(2)
C6	1011(4)	544(4)	887(3)
C7	588(4)	−249(4)	1145(3)
C8	929(4)	−1078(4)	951(3)
C9	1715(4)	−1105(4)	474(3)
C10	2103(3)	−288(4)	240(3)
C11	2127(4)	−1925(3)	228(3)
C21	3644(3)	2310(3)	886(3)
C22	3883(4)	2159(3)	1777(3)
C23	4678(4)	2606(3)	2326(3)
C24	5271(4)	3233(4)	2017(3)
C25	5066(3)	3415(3)	1152(3)
C26	4261(4)	2959(3)	595(3)
C27	3270(4)	1477(3)	2172(2)
C28	6173(4)	3695(4)	2620(3)
C29	4107(4)	3162(3)	−367(3)
C30	8009(8)	4758(6)	755(6)
C31	8553(7)	4271(6)	1414(5)

Table 3. Fractional Atomic Coordinates (×10^4) for Complex 2

atom	x/a	y/b	z/c
Fe1	0	1706.5(7)	1666.7
S1	2739(3)	367(4)	3078(1)
O1	−1900(3)	1989(3)	1886(1)
O2	−3304(4)	2222(5)	2566(1)
O3	1182(5)	0	3333
N1	366(4)	2073(3)	2579(1)
N2	1590(4)	691(4)	1583(1)
C1	1692(6)	3606(6)	2769(2)
C2	1167(9)	3936(7)	3323(2)
C3	−505(9)	3306(10)	3253(2)
C4	−1082(6)	1967(5)	2826(2)
C5	−2192(5)	2071(5)	2399(2)
C6	3158(6)	1488(7)	1516(2)
C7	4086(7)	745(10)	1470(3)
C8	3313(10)	−841(11)	1486(2)
C9	1660(9)	−1759(8)	1565(2)
C10	855(5)	−915(5)	1624(2)
C11	811(8)	−3461(7)	1627(4)
C12	4202(5)	1343(7)	3636(2)

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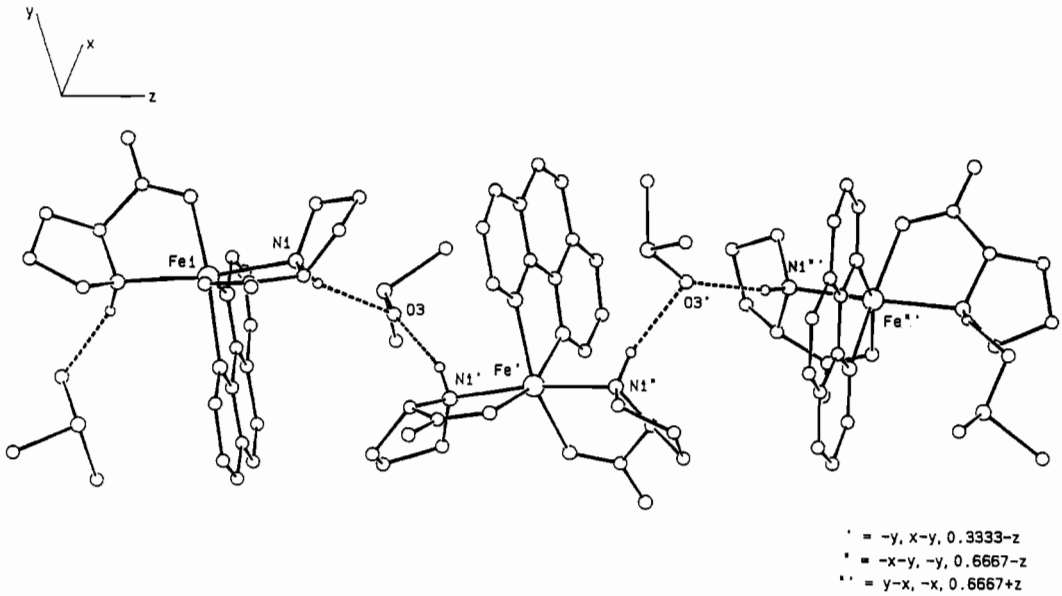

Figure 2. Hydrogen-bonded polymeric form of **2** with DMSO.

Table 4. Fractional Atomic Coordinates ($\times 10^4$) for Complex 3

atom	*x/a*	*y/b*	*z/c*
Fe1	0	1707.1(9)	−1666.7
S1	−2365(4)	−2746(4)	251(2)
O1	−1885(4)	2008(4)	−1884(2)
O2	−3306(6)	2239(8)	−2561(2)
O3	−1190(7)	−1190(7)	0
N1	373(5)	2077(4)	−2579(2)
N2	1571(5)	680(6)	−1593(2)
C1	1684(9)	3596(9)	−2785(3)
C2	1192(15)	3946(12)	−3322(4)
C3	−454(15)	3329(16)	−3252(4)
C4	−1103(9)	1978(8)	−2828(3)
C5	−2190(7)	2060(6)	−2390(3)
C6	3163(9)	1484(9)	−1528(3)
C7	4086(12)	750(16)	−1474(4)
C8	3337(15)	−821(17)	−1479(4)
C9	1673(13)	−1759(11)	−1565(3)
C10	853(8)	−908(7)	−1620(2)
C11	757(20)	−3495(12)	−1633(9)
C12	−4204(10)	−2865(11)	289(4)

Table 5. Selected Bond Distances (Å) and Angles (deg) for Complex 1[a]

Fe1–N1	2.155(4)	N1–C10	1.361(7)
Fe1–C21	2.063(4)	C21–C22	1.402(7)
N1–C6	1.328(7)	C21–C26	1.403(7)
C21–Fe1–C21′	125.5(2)	Fe1–N1–C6	127.1(4)
N1–Fe1–C21′	105.6(2)	C6–N1–C10	117.8(4)
N1–Fe1–C21	116.9(2)	Fe1–C21–C26	118.8(3)
N1–Fe1–N1′	76.0(2)	Fe1–C21–C22	126.2(3)
Fe1–N1–C10	115.1(3)	C22–C21–C26	114.9(4)

[a] Primes indicate the equivalent coordinates $0.5 - x, y, -z$.

Proline, phenylalanine, and tryptophan proved suitable and these reacted to give complexes **2**–**7** in high yield. In the case of valine, the reaction only proceeded at reflux temperature. $[Fe_2(Mes)_4]$ can also be used in reaction 1, however, the resulting amino acid products tend to be insoluble and are probably polymeric. The subsequent addition of phenanthroline breaks the polymers up to the same monomeric species obtained from reaction 1.

The solubilities of the complexes was low and varied according to the size of the amino acid substituents. Complexes **4** and **5** were only slightly soluble in THF while **2**, **3**, and **6**–**8** could be only dissolved in DMSO. The role of the solvent is, very probably, to break down a polymeric form derived from strong hydrogen bond interactions, by way of the solvent remaining hydrogen-bonded in the structure, as shown in the structures of the solvated

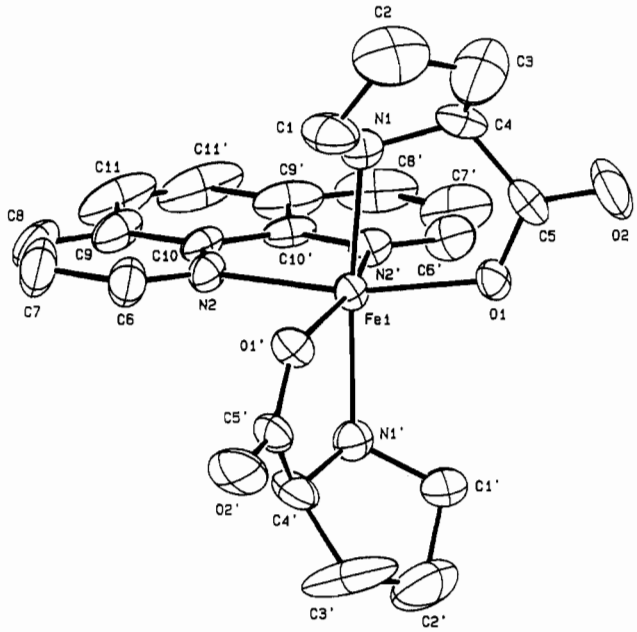

Figure 3. ORTEP drawing for complex **2** (30% probability ellipsoids).

forms of **2** and **3** shown in Figure 2. By layering DMSO solutions of [Fe(L-Pro)$_2$(phen)], **2**, and [Fe(D-Pro)$_2$(phen)], **3**, with Et_2O and THF and allowing the solvents to diffuse slowly over several days, we obtained crystals suitable for X-ray analysis. The structures of complexes **2** and **3** are shown in Figures 3 and 4, and selected structural parameters are reported in Table 6.

Complexes **2** and **3** have the same cell parameters but different spatial arrangements belonging to the enantiomorph space groups $P3_121$ and $P3_221$ respectively. The handedness of the two space groups is consistent with the known configuration of the chiral ligand. They consist of the packing of [Fe(prolinato)$_2$(phen)] units and DMSO molecules joined together by NH···O hydrogen bonds (vide infra) (prolinato = L-prolinato for complex **2** and D-prolinato for complex **3**). The geometries of the two complex molecules, which are nonsuperimposable mirror images of one another, are very close, so they will be described together indicating in brackets the values referred to complex **3**. The [Fe(prolinato)$_2$(phen)] units possess a crystallographically imposed C_2 symmetry, the C_2 axis running through the iron atom and bisecting the phen molecule as observed in complex **1**. The iron atom is six-coordinated by four nitrogen and two oxygens. The one

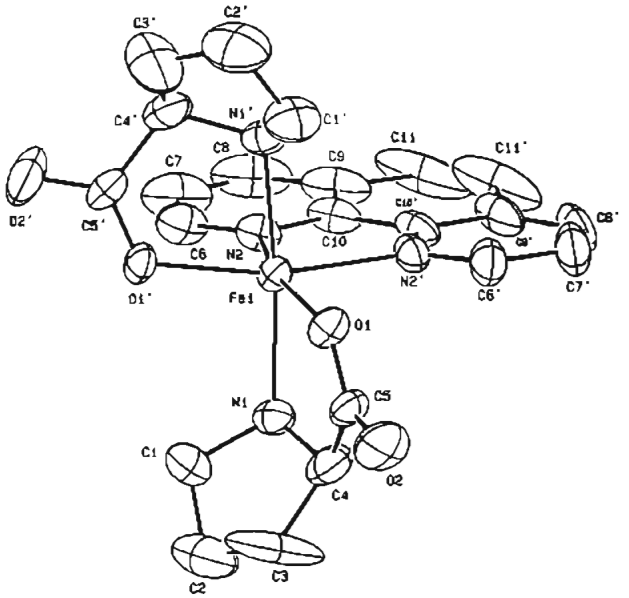

Figure 4. ORTEP drawing for complex **3** (30% probability ellipsoids).

Table 6. Selected Bond Distances (Å) and Angles (deg) for Complexes **2** and **3**[a]

	complex	
	2	**3**
Fe1–O1	2.054(3)	2.055(5)
Fe1–N1	2.195(2)	2.205(5)
Fe1–N2	2.207(5)	2.204(7)
O1–C5	1.262(5)	1.249(9)
O2–C5	1.221(7)	1.246(10)
N1–C1	1.463(5)	1.467(7)
N1–C4	1.473(7)	1.507(10)
N2–C6	1.322(6)	1.345(9)
N2–C10	1.349(6)	1.336(8)
C1–C2	1.500(8)	1.464(14)
C2–C3	1.423(12)	1.406(19)
C3–C4	1.514(9)	1.519(14)
C4–C5	1.515(8)	1.513(11)
N2–Fe1–N2′	75.1(1)	74.3(2)
N1–Fe1–N2′	93.4(1)	94.1(1)
N1–Fe1–N2	93.9(1)	93.3(2)
N1–Fe1–N1′	170.7(1)	170.7(1)
O1–Fe1–N2′	88.3(1)	89.2(2)
O1–Fe1–N2	161.7(1)	161.5(2)
O1–Fe1–N1′	95.5(1)	95.3(2)
O1–Fe1–N1	79.1(1)	79.2(2)
O1–Fe1–O1′	109.1(1)	108.2(1)
Fe1–O1–C5	119.7(3)	119.6(4)
Fe1–N1–C4	108.1(3)	107.8(4)
Fe1–N1–C1	117.2(2)	118.9(4)
C1–N1–C4	105.6(3)	104.5(5)
Fe1–N2–C10	114.9(3)	115.9(5)
Fe1–N2–C6	127.0(3)	126.8(5)
C6–N2–C10	118.0(5)	117.3(6)
N1–C1–C2	105.5(4)	107.8(7)
C1–C2–C3	103.8(4)	103.3(8)
C2–C3–C4	107.3(7)	109.8(12)
N1–C4–C3	106.0(5)	103.7(8)
C3–C4–C5	111.2(4)	114.4(7)
N1–C4–C5	114.1(4)	112.9(6)
O2–C5–C4	119.0(4)	117.2(6)
O1–C5–C4	117.0(4)	118.6(7)
O1–C5–O2	124.0(4)	124.1(7)

[a] Primes refer to transformations of $-x, y - x, 0.3333 - z$ and $-x, y - x, -0.3333 - z$ for complexes **2** and **3**, respectively.

independent prolinato ion acts as bidentate chelating ligand, contributing one carboxyl oxygen and the nitrogen atom of the pyrrolidine ring to the coordination which could be described as a distorted octahedron. The molecular helicity is Δ for the L-prolinato derivative and Λ for the D-prolinato derivative. The

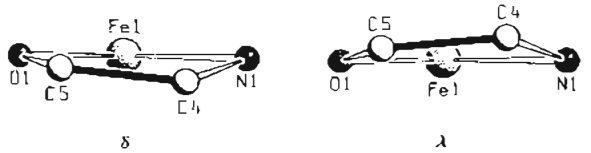

Figure 5. δ and λ conformations in complexes **2** and **3**, respectively.

bidentate prolinato ligand gives rise to a five-membered chelate ring which is not planar, the C4 and C5 carbon atoms being displaced by 0.280(4) [0.290(7)] and 0.136(4) Å [0.164(5) Å], respectively, from the plane through Fe, N1, and O1. Although on the same side, the dissymmetry of these displacements gives rise to a ring conformation which is δ for complex **2** and λ for complex **3**, as displayed in Figure 5. Considering the whole structure, complex **2** represents the δδ conformer of the Δ configuration and complex **3** represents the λλ conformer of the Λ configuration. In addition, the arrangement of the ligands about the metal ion corresponds to the *O,O-mer* diastereoisomer for both complexes. The "*O,O-mer*" is used to indicate the two oxygen atoms from the two symmetry-related prolinato anions lying on the plane of the equatorial phen molecule, the nitrogen atoms being at the opposite apices of the octahedron. The Fe–N(prolinato) bond distances in complexes **2** and **3** are not significantly different (Table 6). They are in the upper end of the range observed for Fe–N (N from secondary amines) quoted in the literature [mean value 2.164(78) Å over 44 structures].[8] The Fe–O bond distances are practically the same and are in good agreement with Fe–O (alkyl carboxylate) [terminal, O_2-$CC(sp^3)$] bond distances [mean value 2.038(69) over 40 structures].[8] The Fe–N(phen) bond distances are significantly longer than those observed in complex **1** as a consequence of the increased coordination number of iron.

Bond distances and angles in the prolinato anions in the two complexes **2** and **3** are very close. A comparison with the free L-proline[9] is not useful since the residual *R* for the X-ray structure of free L-proline was 0.169. However they are in good agreement with those observed *e.g.* in pentaaquobis(hydroxy-L-prolinato)-calcium.[10] Significant differences concern the C–O bond distances that are significantly different in **2**, indicating the double bond localized on the C5–O2 bond, while they are not significant in **3**, where the accuracy of the structure is lower. The shortening of the C2–C3 bond distances reflects the high thermal motion affecting these atoms. The pyrrolidine ring is puckered. The planes N1,C1,C4,C3 and C1,C2,C3 make an angle of 33.1(4)° [31.9(7)°]. The COO group forms a dihedral angle of 54.2(2)° [54.8(3)°] with the mean plane of the pyrrolidine ring. The packing is mainly determined by a NH···O hydrogen bond involving the amino acidic nitrogen and the oxygen from DMSO: N1–H1, 0.91 Å [0.91 Å]; N1···O3, 3.069(4) Å [3.083(8) Å]; H1···O3, 2.21 Å [2.22 Å]; N1-H1···O3, 158° [158°].

Optical rotations were measured for all of the complexes; however, due to their intense blue color, good light transmission was only possible using the Hg 436-nm line. The angles of rotation can be compared with the values for the uncomplexed amino acids $[\alpha]_{436}^{20}$: L-pro, −179°; D-pro, +180°; L-phe, −65°; D-phe, +72°; L-trp, −55°; L-val, +15°).

We are currently investigating the reactions of these compounds, as well as extending the methodology to other metals. Preliminary results showed that these complexes are readily oxidized to iron(III) forms.

Experimental Section

General Procedure. All operations were carried out under an atmosphere of purified nitrogen using modified Schlenk techniques or in a Braun drybox. Solvents were dried and distilled before use by standard

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Table 7. Summary of Analytical Results

formula	yield, %	found C	found H	found N	calcd, % C	calcd, % H	calcd, % N	$[\alpha]^{20}_{436}$, deg	ν(CO), cm^{-1}
Fe(L-Pro)$_2$(phen)	95	53.22	5.96	10.26	53.14	5.57	10.33	−32	1616
Fe(D-Pro)$_2$(phen)	92	52.21	5.82	9.88	53.14	5.57	10.33	+31	1624
Fe(L-Phe)$_2$(phen)	98	64.01	5.12	9.73	63.84	5.00	9.89	−52	1620
Fe(D-Phe)$_2$(phen)	89	63.54	5.31	10.01	63.84	5.00	9.89	+65	1624
Fe(DL-Phe)$_2$(phen)	90	64.26	5.48	9.53	63.84	5.00	9.89	0	1593, 1633
Fe(L-Trp)$_2$(phen)	98	62.90	5.30	12.07	63.56	4.71	13.08	−54	1594
Fe(L-Val)$_2$(phen)	81	55.12	6.20	11.04	56.42	6.03	11.96	−79	1574, 1624

methods. 1,10-Phenanthroline monohydrate (Fluka) was dried by dissolving in anhydrous THF, which was then repeatedly distilled back and forth into a flask containing $LiAlH_4$, and then the anhydrous compound was recrystallized from THF/hexane. α-Amino acids (Fluka) were dried by stirring in refluxing anhydrous THF for several hours, after which traces of water were distilled off with the THF. The $[\alpha]^{20}_{436}$ measurements were made with a Perkin-Elmer 241 polarimeter. Magnetic measurements were carried out at 293 K using a Gouy balance. Infrared spectra were recorded on a Perkin-Elmer 1600 FT spectrometer. Analytical data for complexes **1–8** are summarized in Table 7.

Synthesis of [Fe(Mes)$_2$(phen)], 1. To a suspension of $FeCl_2$·1.5THF (16.56 g, 70.5 mmol) in THF (300 mL) and dioxane (75 mL) was added dropwise at −30 °C a THF solution of MesMgBr (141.0 mmol), and upon warming of the mixture to room temperature, a red-brown solution formed as white MgBrCl·dioxane precipitated. After being stirred for a total of 3 h at room temperature, the solution was filtered and the filtrate evaporated to dryness. The residue was redissolved in Et_2O (300 mL) and the red solution filtered to remove additional traces of insoluble MgBrCl·dioxane. To the Et_2O filtrate was added anhydrous 1,10-phenanthroline (12.52 g, 69.57 mmol), and over 6 h, a purple microcrystalline solid precipitated, which was collected by filtration, washed with small quantities of Et_2O, and dried in vacuo (22.2 g, 66%). Crystals used for X-ray analysis not dried in vacuo contain Et_2O of crystallization. Anal. Calcd for $C_{30}H_{30}FeN_2$: C, 75.95; H, 6.37; N, 5.90. Found: C, 74.91; H, 6.32; N, 6.08.

Synthesis of [Fe(L-Pro)$_2$(phen)]·DMSO, 2·DMSO. To a THF (100 mL) solution of Fe(Mes)$_2$(phen) (2.98 g, 6.30 mmol) was added L-proline (1.45 g, 12.61 mmol). After 72 h, the purple solution became clear and a dark blue precipitate had formed. The solid was collected by filtration, washed with small quantities of THF, and dried under vacuum giving **2** (95%). The product was recrystallized by dissolving in DMSO (30 mL), and then after filtration to remove some undissolved material, the dark blue solution was layered with Et_2O (50 mL) and THF (10 mL) and microcrystalline **2**·DMSO precipitated over 48 h. Crystals suitable for X-ray analysis were obtained by this method. Anal. Calcd for $C_{24}H_{30}FeN_4O_5S$: C, 53.14; H, 5.57; N, 10.33. Found: C, 53.22; H, 5.96; N, 10.26. IR (Nujol): ν(CO) 1616 cm^{-1}. μ: 5.41 μ_B at 293 K. $[\alpha]^{20}_{436}$: −32°.

Synthesis of [Fe(D-Pro)$_2$(phen)]·DMSO, 3·DMSO. To a THF (100 mL) solution of Fe(Mes)$_2$(phen) (2.061 g, 4.35 mmol) was added D-proline (1.00 g, 8.70 mmol). After 72 h, the purple solution became clear and a dark blue precipitate had formed. The solid was collected by filtration, washed with small quantities of THF, and dried under vacuum giving **3** (92%). The product was recrystallized by dissolving in DMSO (25 mL), and then after filtration to remove some undissolved material, the dark blue solution was layered with Et_2O (40 mL) and THF (10 mL) and microcrystalline **3**·DMSO precipitated over 48 h. Crystals suitable for X-ray analysis were obtained by this method. Anal. Calcd for $C_{24}H_{30}FeN_4O_5S$: C, 53.14; H, 5.57; N, 10.33. Found: C, 52.21; H, 5.82; N, 9.88. IR (Nujol): ν(CO) 1624 cm^{-1}. μ: 5.03 μ_B at 293 K. $[\alpha]^{20}_{436}$: +31°.

Synthesis of [Fe(L-Phe)$_2$(phen)], 4. To a THF (100 mL) solution of Fe(Mes)$_2$(phen) (2.086 g, 4.40 mmol) was added L-phenylalanine (1.645 g, 9.97 mmol). After 72 h, a blue solid and solution was obtained. The solid was collected by filtration, washed with small quantites of Et_2O, and dried under vacuum giving **4** (2.434 g, 98%). The product was recrystallized by slow extraction into refluxing THF. Anal. Calcd for $C_{30}H_{28}FeN_4O_4$: C, 63.84; H, 5.00; N, 9.89. Found: C, 64.01; H, 5.12; N, 9.73. IR (Nujol): ν(CO) 1620 cm^{-1}. μ: 5.15 μ_B at 293 K. $[\alpha]^{20}_{436}$: −52°.

Synthesis of [Fe(D-Phe)$_2$(phen)], 5. To a THF (100 mL) solution of Fe(Mes)$_2$(phen) (2.354 g, 4.97 mmol) was added D-phenylalanine (1.643 g, 9.96 mmol). After 72 h, a blue solid and solution was obtained. The solid was collected by filtration, washed with small quantities of Et_2O, and dried under vacuum giving **5** (2.481 g, 89%). The product was recrystallized by slow extraction into refluxing THF. Anal. Calcd for $C_{30}H_{28}FeN_4O_4$: C, 63.84; H, 5.00; N, 9.89. Found: C, 63.54; H, 5.31; N, 10.01. IR (Nujol): ν(CO) 1624 cm^{-1}. μ: 5.27 μ_B at 293 K. $[\alpha]^{20}_{436}$: +65°.

Synthesis of [Fe(DL-Phe)$_2$(phen)], 6. To a THF (100 mL) solution of Fe(Mes)$_2$(phen) (2.425 g, 5.12 mmol) was added DL-phenylalanine (1.684 g, 10.21 mmol). After 72 h, the purple solution became clear and a blue solid had precipitated, which was collected by filtration, washed with small quantities of Et_2O, and dried under vacuum giving **6** (2.600 g, 90%). Anal. Calcd for $C_{30}H_{28}FeN_4O_4$: C, 63.84; H, 5.00; N, 9.89. Found: C, 63.26; H, 5.48; N, 9.53. IR (Nujol): ν(CO) 1593, 1633 cm^{-1}. μ: 5.21 μ_B at 293 K. $[\alpha]^{20}_{436}$: 0°.

Synthesis of [Fe(L-Trp)$_2$(phen)], 7. To a THF (100 mL) solution of Fe(Mes)$_2$(phen) (3.212 g, 6.78 mmol) was added L-tryptophan (2.624 g, 12.86 mmol). After 72 h, the purple solution became clear and a violet precipitate had formed, which was collected by filtration, washed with small quantities of Et_2O, and dried under vacuum giving **7** (4.274 g, 98%). Anal. Calcd for $C_{34}H_{30}FeN_6O_4$: C, 63.56; H, 4.71; N, 13.08. Found: C, 63.32; H, 4.73; N, 12.96. IR (Nujol): ν(CO) 1594 cm^{-1}. μ: 5.35 μ_B at 293 K. $[\alpha]^{20}_{436}$: −54°.

Synthesis of [Fe(L-Val)$_2$(phen)], 8. To a THF (100 mL) solution of Fe(Mes)$_2$(phen) (4.74 g, 10.06 mmol) was added L-valine (2.354 g, 20.12 mmol). After 72 h of stirring in refluxing THF, the purple solution became clear and a dark blue precipitate had formed. The solvent was evaporated to dryness and the residue extracted with DMSO (40 mL), which was then filtered to remove some undissolved material. The dark blue solution was layered with Et_2O (60 mL) and THF (20 mL) resulting in the precipitation after 48 h of **8** (81%). Anal. Calcd for $C_{22}H_{28}FeN_4O_4$: C, 56.42; H, 6.03; N, 11.96. Found: C, 55.12; H, 6.20; N, 11.04. IR (Nujol): ν(CO) 1574, 1624 cm^{-1}. μ: 5.20 μ_B at 293 K. $[\alpha]^{20}_{436}$: −79°.

X-ray Crystallography. The crystals selected for study were mounted in glass capillaries and sealed under nitrogen. The reduced cells were obtained with use of TRACER.[11] Crystal data and details associated with data collection are given in Tables 1 and SI. Data were collected at room temperature (295 K) on a single-crystal diffractometer. For intensities and background the profile measurement technique[12] was used. The structure amplitudes were obtained after the usual Lorentz and polarization corrections,[13] and the absolute scale was established by the Wilson method.[14] The crystal quality was tested by ψ scans showing that crystal absorption effects could be neglected for all complexes. The function minimized during the least-squares refinement was $\sum w(\Delta F^2)^2$. Weights were applied according to the scheme $w = 1/[\sigma^2(F_o^2) + (gP)^2]$ with $P = (F_o^2 + 2F_c^2)/3$ (g = 0.0331, 0, and 0.0844 for **1–3**, respectively). Anomalous scattering corrections were included in all structure factor calculations.[15b] Scattering factors for neutral atoms were taken from ref 15 a for non-hydrogen atoms and form ref 16 for H. No correction for secondary extinction was deemed necessary. Structure solutions were based on the observed reflections [$I > 2\sigma(I)$], while the structure refinements were based on all reflections.

Complex 1. The structure was solved by the heavy-atom method starting from a three-dimensional Patterson map. Refinement was done

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(15) (a) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, p 99. (b) *Ibid.*, p 149.
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by full-matrix least-squares first isotropically and then anisotropically for non-H atoms. The hydrogen atoms, except those associated with the Et_2O solvent molecule, were located from difference Fourier maps and introduced in the subsequent refinements as fixed atom contributions with isotropic U's fixed at 0.12 Å^2.

Complexes 2 and 3. The structures were solved by the heavy-atom method starting from a three-dimensional Patterson map. Refinement was done by full-matrix least-squares first isotropically and then anisotropically for all the non-H atoms. In both complexes the C2, C3, C8, C9, and C10 carbons were found to be affected by high thermal motion. Attempts to define a model in terms of statistical disorder were unsuccessful, resulting in reliable geometrical parameters. The sulfur atom of the DMSO solvent molecule was found to be statistically distributed in two positions around a C_2 axis corresponding to the enantiomeric forms of DMSO. The hydrogen atoms were located from difference Fourier maps and introduced in the subsequent refinements as fixed atom contributors with isotropic U's fixed at 0.12 Å^2. The hydrogens associated with the DMSO solvent molecules were ignored.

All calculations were performed by using SHELX76[17] for the early stages of the structure determination and SHELXL92[18] for the structure refinements. The final difference maps showed no usual feature, with no significant peak above the general background. Final atomic coordinates are listed in Tables 2–4 for non-H atoms and in Tables SII–SIV for hydrogens. Thermal parameters are given in Tables SV–SVII; bond distances and angles, in Tables SVIII–SX.[19]

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Supplementary Material Available: Tables giving crystal data and details of the structure determination, bond lengths, bond angles, anisotropic thermal parameters, and hydrogen atom locations (11 pages). Ordering information is given on any current masthead page.

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(19) See paragraph at the end of paper regarding supplementary material.