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Polyhedron 23 (2004) 15-21



Syntheses and crystal structures of ferrocene-containing enaminones and their copper complexes

Yao-Cheng Shi^{a,*}, Hua-Mei Yang^a, Wen-Bin Shen^b, Chao-Guo Yan^a, Xiao-Ya Hu^a

^a School of Chemistry, Yangzhou University, Yangzhou 225002, PR China ^b Analytical Center, China Pharmaceutical University, Nanjin 210009, PR China

Received 2 July 2003; accepted 29 August 2003

Abstract

Six ferrocene-containing enaminones $[C_5H_5FeC_5H_4C(O)CH = C-(NHAr)R]$ (HL¹, R = CH₃, Ar = C₆H₅; HL², R = CH₃, Ar = 2-CH₃C₆H₄; HL³, R = CH₃, Ar = 2,6-(CH₃)₂C₆H₃; HL⁴, R = C₆H₅, Ar = C₆H₅; HL⁵, R = C₆H₅, Ar = 2-CH₃C₆H₄; HL⁶, R = C₆H₅, Ar = 2,6-(CH₃)₂C₆H₃) and their copper(II) complexes (I, L₂¹Cu·2H₂O; II, L₂²Cu; III, L₂³Cu; IV, L₂⁴Cu·2H₂O; V, L₂⁵Cu·2H₂O) have been synthesized and characterized by elemental analyses, ¹HNMR, IR and UV spectroscopies. Their structures have been determined by the X-ray crystallography of enaminone HL⁶ and complex I.

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Keywords: Ferrocene; Enaminone; Ligand; Copper; Complex; X-ray crystallography

1. Introduction

In the last few decades enaminones and enaminecarbaldehydes have been widely investigated because of their applications in the synthesis of heterocyclic compounds [1] and plentiful reaction chemistry [2] and coordination chemistry [3]. Therefore, enaminones of the type [R'C(O)CHC(NHAr)R] constitute an important class. Recently non-metallocene complexes of Group IV metals have attracted much interest as possible alternatives for olefin polymerization catalysts using N₄macrocycles, porphrins, tripodal amides, mixed cyclopentadienyl-amides and Schiff bases as spectator ligands [5–7]. Because the anions $[R'C(O)CHC(NAr)R]^{-}$ generated from the above enaminones offer potential isoelectronic alternatives to the cyclopentadienyl-based anion and can be used as good chelating ligands for copper complexes that exhibit catalytic activity [3,8], organometallic enaminones of the new type $[C_5H_5FeC_5]$ $H_4C(O)CH = C(NHAr)R$ have been studied. To our knowledge, so far no article on organometallic enami-

nones has appeared, and herein we report the syntheses and structures of the ferrocenyl enaminones and their copper complexes.

2. Experimental

2.1. Reagents and general procedures

All chemicals used were of reagent grade. Toluene and THF were distilled from Na/benzophenone under dinitrogen atmosphere. Absolute ethanol for sodium ethoxide was distilled from Na/diethyl phthalate. DMF, ethyl acetate and ethyl benzoate were redistilled before use. Other commerial chemicals were used without further purification. Acetylferrocene was synthesized from ferrocene according to the literature method [9]. Progress of the reactions was monitored by TLC. ¹H NMR spectra were determined with a Bruker Avance 500 spectrometer using TMS as external standard in CDCl₃. IR spectra were recorded on a Perkin-Elmer 402 as KBr disks in the range of 400–4000 cm⁻¹. UV spectra were measured with a Shimadzu UV-240 spectrometer using a solution in DMF. Analyses for C, H and N were performed on an Elementa Vario EL III instrument.

^{*}Corresponding author. Tel.: +86-514-7857939; fax: +86-514-7857939.

E-mail address: yzssyc@yzcn.net (Y.-C. Shi).

Melting points were measured on a Yanagimoto apparatus and were uncorrected.

2.2. Syntheses of enaminones

2.2.1. Syntheses of β -diketones 1 and 2

Modified literature syntheses were used [10,11]. A solution of sodium ethoxide (8.85 g, 130 mmol), acetyl-ferrocene (16.42 g, 72 mmol) and ethyl acetate (11.45 g, 130 mmol) in 60 ml of THF was refluxed under nitrogen for 2 h. The yellow solid was filtered, washed with THF and acidified with aqueous acetic acid to give the β -di-ketone 1 (16.14 g, 83%) as a red solid. M.p. 97 °C (lit: 97–97.5 °C) [10]. UV (nm, in DMF): $\lambda_{max}(\varepsilon \times 10^4)$ 261 (1.02), 308 (1.12).

The similar reaction of sodium ethoxide (4.08 g, 60 mmol), acetylferrocene (7.98 g, 35 mmol) and ethyl benzoate (5.56 g, 37 mmol) in 60 ml of THF for 2 h after the above-mentioned workup and extraction with CH₂Cl₂ (three times, each 20 ml) gave the combined organic layer. The mixture was dried with anhydrous CaCl₂ and then the solvent of the filtrate was removed to give a purple–red oil, which was separated with the eluant (CH₂Cl₂: petroleum ether, 2:1) by vacuum liquid chromatography (VLC). A main band was collected to afford the β -diketone **2** (5.81 g, 50%) as a purple–red solid. M.p. 106 °C (lit: 106–107 °C) [11]. UV (nm, in DMF): $\lambda_{max}(\varepsilon \times 10^4)$ 268 (0.85), 332 (0.64), 360 (0.65).

2.2.2. Syntheses of enaminones

 $[C_5H_5FeC_5H_4C(O)CH = C(NHAr)CH_3](Ar = C_6H_5,$ HL^{1}). Aniline (1.86 g, 20 mmol) was added to a solution of β -diketone 1 [C₅H₅FeC₅H₄C(O)CH₂C(O) CH₃] (2.7 g, 10 mmol) and a catalytic trace amount of p-TsOH $(\approx 10 \text{ mg})$ in 20 ml of toluene, and then the mixture was refluxed with a Dean-Stark apparatus to remove water for 2 h. The solvent was evaporated under vacuum, and the residue was recrystallized from petroleum ether (60-90 °C) to afford 2.76 g (80%) of HL¹ as a red crystalline solid. M.p. 120-121 °C. Anal. Found: C, 69.60; H, 5.52; N, 3.72. Calc. for C₂₀H₁₉NFeO: C, 69.58; H, 5.55; N, 4.06%. IR (KBr disk): v(NH) 3084 (s), v(C=O) and v(C = C) 1582 (vs, br) cm⁻¹. UV (nm, in DMF): $\lambda_{\max}(\varepsilon \times 10^4)$ 259 (8.7), 275 (1.5) (B-band); 328 (1.9) (K-band). ¹H NMR (CDCl₃): δ 2.15 (s, 3H, CH₃), 4.24 (s, 5H, C₅H₅), 4.58 (s, 2H, 2 (H³, H⁴) of C₅H₄ ring), 4.83 $(s, 2H, 2 (H^2, H^5) \text{ of } C_5H_4 \text{ ring}), 5.54 (s, 1H, CH), 7.10-$ 7.37 (m, 5H, C₆H₅), 12.64 (s, 1H, NH).

[C₅H₅FeC₅H₄C(O)CH = C(NHAr)CH₃] (Ar = 2-CH₃ C₆H₄, **HL**²). The similar reaction of 2-methylaniline (2.14 g, 20 mmol) and β-diketone 1 (10 mmol) afforded 2.83 g (80%) of **HL**² as a red crystalline solid. M.p. 96–97 °C. *Anal.* Found: C, 70.24; H, 5.70; N, 3.85. Calc. for C₂₁H₂₁FeNO: C, 70.21; H, 5.89; N, 3.90%. IR (KBr disk): ν (NH) 3080 (s), ν (C=O) 1601 (vs), ν (C=C) 1554 (vs) cm⁻¹. UV (nm, in DMF): $\lambda_{max}(\varepsilon \times 10^4)$ 274 (0.9) (B-band), 333 (1.2) (K-band). ¹H NMR (CDCl₃): δ 1.99 (s, 3H, CH₃), 2.33 (s, 3H, CH₃), 4.21 (s, 5H, C₅H₅), 4.41 (s, 2H, 2 (H³, H⁴) of C₅H₄ ring), 4.79 (s, 2H, 2 (H², H⁵) of C₅H₄ ring), 5.54 (s, 1H, CH), 7.12–7.27 (m, 4H, C₆H₄), 12.44 (s, 1H, NH).

[C₅H₅FeC₅H₄C(O)CH = C(NHAr)CH₃] (Ar = 2,6-(CH₃)₂C₆H₃, **HL**³). The similar reaction of 2,6-dimethylaniline (2.42 g, 20 mmol) and β-diketone **1** (10 mmol) afforded 2.99 g (80%) of **HL**³ as a red crystalline solid. M.p. 114–116 °C. *Anal.* Found: C, 70.81; H, 6.04; N, 3.27. Calc. for C₂₂H₂₃FeNO: C, 70.79; H, 6.21; N, 3.75%. IR (KBr disk): v(NH) 3079 (w), v(C=O) 1603 (vs), v(C=C) 1553 (vs) cm⁻¹. UV (nm, in DMF): $\lambda_{max}(\varepsilon \times 10^4)$ 265 (1.51) (B-band), 330 (1.36) (K-band). ¹H NMR (CDCl₃): δ 1.73 (s, 3H, CH₃), 2.26 (s, 6H, 2CH₃ of benzene ring), 4.21 (s, 5H, C₅H₅), 4.41 (s, 2H, 2 (H³, H⁴) of C₅H₄ ring), 4.82 (s, 2H, 2 (H², H⁵) of C₅H₄ ring), 5.57 (s, 1H, CH), 7.10–7.15 (m, 3H, C₆H₃), 12.03 (s, 1H, NH).

[C₅H₅FeC₅H₄C(O)CH = C(NHAr)C₆H₅] (Ar = C₆H₅, HL⁴). The similar reaction of aniline (0.93g, 10 mmol) and β-diketone **2** [C₅H₅FeC₅H₄C(O)CH₂C(O) C₆H₅] (1.66 g, 5 mmol) afforded 1.71 g (84%) of HL⁴ as a deep red crystalline solid. M.p. 118–120 °C. *Anal.* Found: C, 73.29; H, 5.00; N, 3.02. Calc. for C₂₅H₂₁ FeNO: C, 73.72; H, 5.20; N, 3.44%. IR (KBr disk): v(NH) 3087 (s), v(C=O) 1589 (vs), v(C=C) 1567 (vs) cm⁻¹. UV (nm, in DMF): $\lambda_{max}(\varepsilon \times 10^4)$ 369 (1.06) (K-band). ¹H NMR (CDCl₃): δ 4.25 (s, 5H, C₅H₅), 4.57 (s, 2H, 2 (H³, H⁴) of C₅H₄ ring), 4.87 (s, 2H, 2 (H², H⁵) of C₅H₄ ring), 5.77 (s, 1H, CH), 6.75–7.13 (3m, 5H, NC₆H₅), 7.27–7.44 (m, 5H, C₆H₅), 12.43 (s, 1H, NH).

[C₅H₅FeC₅H₄C(O)CH = C(NHAr)C₆H₅] (Ar = 2-CH₃C₆H₄, **HL**⁵). The similar reaction of 2-methylaniline (1.07 g, 10 mmol) and β-diketone **2** (5 mmol) afforded 1.71 g (81%) of **HL**⁵ as a light red crystalline solid. M.p. 138–140 °C. *Anal.* Found: C, 73.98; H, 5.22; N, 2.88. Calc. for C₂₆H₂₃FeNO: C, 74.12; H, 5.50; N, 3.32%. IR (KBr disk): *v*(NH) 3082 (s), *v*(C=O) 1591 (vs), *v*(C=C) 1567 (vs) cm⁻¹. UV (nm, in DMF): $\lambda_{max}(\varepsilon \times 10^4)$ 274 (1.32) (B-band), 369 (1.03) (K-band). ¹H NMR (CDCl₃): δ 2.48 (s, 3H, CH₃), 4.27 (s, 5H, C₅H₅), 4.50 (s, 2H, 2 (H³, H⁴) of C₅H₄ ring), 4.90 (s, 2H, 2 (H², H⁵) of C₅H₄ ring), 5.70 (s, 1H, CH), 6.40–7.50 (4m, 9H, (C₆H₄, C₆H₅)), 12.26 (s, 1H, NH).

[C₅H₅FeC₅H₄C(O)CH = C(NHAr)C₆H₅] (Ar = 2,6-(CH₃)₂C₆H₃, **HL**⁶). The similar reaction of 2,6-dimethylaniline (1.21 g, 10 mmol) and β-diketone **2** (5 mmol) was refluxed for four days. After removal of the solvent, the deep-red oil obtained was chromatographed on a silica gel column with CH₂Cl₂and petroleum ether (3:1). The second band was collected and further recrystallized from petroleum ether (60–90 °C) afforded 1.31 g (46%) of **HL**⁶ as a deep red crystalline solid. M.p. 153–154 °C. *Anal.* Found: C, 74.89; H, 5.67; N, 2.79. Calc. for C₂₇H₂₅FeNO: C, 74.49; H, 5.79; N, 3.22%. IR (KBr disk): v(NH) 3080 (w), v(C = O) 1586 (vs), v(C = C) 1567(vs) cm⁻¹. UV (nm, in DMF): $\lambda_{max}(\varepsilon \times 10^4) 365$ (1.45) (K-band). ¹H NMR (CDCl₃): δ 2.21 (s, 6H, 2CH₃), 4.24 (s, 5H, C₅H₅), 4.46 (s, 2H, 2 (H³, H⁴) of C₅H₄ ring), 4.87 (s, 2H, 2 (H², H⁵) of C₅H₄ ring), 5.70 (s, 1H, CH), 6.93– 7.33 (2m, 8H, (C₆H₃, C₆H₅)), 12.22 (s, 1H, NH).

2.3. Syntheses of copper complexes

A solution of 1 mmol of the appropriate ligand (except enaminone HL^6) in absolute ethanol (10 ml) was added dropwise to a stirred solution of 0.5 mmol of hydrated copper acetate in the same solvent (10 ml). The mixture was stirred for 24 h at room temperature and then filtered to afford the crude product. The resulting solid was recrystallized from CH_2Cl_2 and petroleum ether to give the corresponding complex.

Complex I as a black solid, yield: 0.335 g (85%). M.p. 201–202 °C (dry sample). *Anal.* Found: C, 60.82; H, 4.71; N, 3.14. Calc. for C₄₀H₄₀N₂O₄Fe₂Cu: C, 60.97; H, 5.12; N, 3.55%. IR (KBr disk): v(OH) 3436 (m, br), v(C = O) 1562 (s), v(C = C) 1513 (vs) cm⁻¹. UV (nm, in DMF): $\lambda_{max}(\varepsilon \times 10^4)$ 275 (2.5), 358 (3.4) (K-band), 450 (0.49) (CT-band).

Complex II as a black red solid, yield: 0.312 g (80%). M.p. 209.5–210.5 °C. *Anal.* Found: C, 64.75; H, 5.21; N, 3.33. Calc. for C₄₂H₄₀N₂O₂Fe₂Cu: C, 64.67; H, 5.17; N, 3.59%. IR (KBr disk): v(C = O) 1561 (s), v(C = C) 1512 (vs) cm⁻¹. UV (nm, in DMF): $\lambda_{max}(\varepsilon \times 10^4)$ 275 (2.9), 355 (4.3) (K-band), 447 (0.50) (CT-band).

Complex **III** as a purple red solid, yield: 0.331 g (82%). M.p. 213–214.5 °C. *Anal.* Found: C, 65.30; H, 5.16; N, 3.04. Calc. for C₄₄H₄₄N₂O₂Fe₂Cu: C, 65.40; H, 5.49; N, 3.47%. IR (KBr disk): v(C=O) 1557 (s), v(C=C) 1513 (vs) cm⁻¹. UV (nm, in DMF): $\lambda_{max}(\varepsilon \times 10^4)$ 278 (2.4), 351 (3.2) (K-band), 447 (0.37) (CT-band).

Complex IV as a black solid, yield: 0.379 g (83%). M.p. 203.5–205 °C (dry sample). *Anal.* Found: C, 65.51; H, 4.47; N, 3.14. Calc. for C₅₀H₄₄N₂O₄Fe₂Cu: C, 65.84; H, 4.86; N, 3.07%. IR (KBr disk): v(OH) 3439 (w, br), v(C = O) 1550 (m), v(C = C) 1509 (vs) cm⁻¹. UV (nm, in DMF): $\lambda_{max}(\varepsilon \times 10^4)$ 379 (3.5) (K-band).

Complex V as a black red solid, yield: 0.376 g (80%). M.p. 222.5–223.5 °C (dry sample). *Anal.* Found: C, 66.85; H, 5.06; N, 3.18. Calc. for $C_{52}H_{48}N_2O_4Fe_2Cu$: C, 66.43; H, 5.15; N, 2.98%. IR (KBr disk): ν (OH) 3430 (w, br), ν (C = O) 1580 (m), ν (C = C) 1513 (vs) cm⁻¹. UV (nm, in DMF): $\lambda_{max}(\varepsilon \times 10^4)$ 378 (2.67) (K-band).

2.4. Crystal structure determinations

Single crystals of enaminone HL^6 for X-ray analysis were obtained by slow evaporation of its solution in CH_2Cl_2 and petroleum ether at room temperature. Single crystals of complex I for structure determination were obtained by further recrystallization from CH_2Cl_2 and ethanol. X-ray data of both compounds were measured on an Enraf–Nonius CAD4 diffractometer using graphite-monochromated Mo K_{α} radiation ($\lambda = 0.71073$ Å) at 293 K. The structures were solved by direct methods and refined by full-matrix least-squares methods based on F^2 with anisotropic thermal parameters for all non-hydrogen atoms [12]. A summary of the data collection and structure refinement parameters is given in Table 1. Selected bond distances (Å) and angles (°) are listed in Tables 2 (enaminone HL⁶) and 3 (complex I).

3. Results and discussion

3.1. Syntheses of enaminones and their complexes

Syntheses of enaminones and their complexes are represented in Schemes 1 and 2. Reaction of the β -diketone 1 or 2 $[C_5H_5FeC_5H_4C(O)CH_2C(O)R]$ (R = CH₃, C_6H_5) and an excess of an appropriate aniline [H₂NAr] $(Ar = Ph, 2-CH_3C_6H_4, 2, 6-(CH_3)_2C_6H_3)$ in the presence of a catalytic trace amount of p-toluenesulfonic acid in refluxing toluene via removal of water using a Dean-Stark apparatus affords the corresponding enaminones in satisfactory yields. For enaminones HL⁴, HL⁵ and HL⁶, in view of the electronic and steric effects of the phenyl and ferrocenyl groups, it may be expected that the anilines attack the carbonyl with the Ph substituent. This conclusion is further supported by X-ray diffraction analysis on the enaminone HL⁶ (see below). Also because of steric hindrance from the N-phenyl and C-phenyl groups, reaction of the β -diketone 2 with 2,6dimethylaniline is incomplete and accordingly enaminone HL⁶ is obtained only in moderate yield. Except HL⁶, each enaminone can react with the copper(II) ion forming the corresponding neutral complex with the release of HOAc. TLC analyses of all the complexes show that each exists as a single isomer. However, because of the steric hindrance of HL⁶, all attempts to synthesize the corresponding complex $L_2^6Cu \cdot xH_2O$ were unsuccessful and the starting materials were recovered.

Analytical data of all the new complexes listed in Section 2 suggest that they may be formulated as $L_2^1Cu \cdot 2H_2O$, L_2^2Cu , L_2^3Cu , $L_2^4Cu \cdot 2H_2O$ and $L_2^5Cu \cdot 2H_2O$, respectively.

3.2. ¹H NMR spectra of enaminones

The ¹H NMR spectral data of the enaminones are presented in Section 2. The spectra of the free ligands display two singlets at δ 4.41–4.58 and 4.79–4.90 ppm, with the integration corresponding to 2H attributed to the H³/H⁴ and H²/H⁵ protons of the substituted cyclopentadienyl ring. Another singlet signal with the integration corresponding to 5H at δ 4.21–4.27 ppm is due

Table 1					
Crystallographic	data	for	HL6	and	I

	HL ⁶	I
Formula	C ₂₇ H ₂₅ FeNO	$C_{40}H_{40}Fe_2N_2O_4Cu$
Formula weight	435.33	787.98
Crystal size (mm)	0.30 imes 0.30 imes 0.20	$0.3 \times 0.3 \times 0.2$
Crystal system	monoclinic	orthorhombic
Space group	<i>P</i> 2 ₁ /c	Pbcn
Unit cell dimensions		
$a(\text{\AA})$	8.3000(17)	12.910(3)
$b(\mathbf{\mathring{A}})$	13.320(3)	19.280(4)
$c(\text{\AA})$	20.410(4)	27.620(6)
$\alpha(^{\circ})$	90.00	90.00
$\beta(^{\circ})$	101.66(3)	90.00
γ(°)	90.00	90.00
$V(\text{\AA}^3)$	2209.9(8)	6875(2)
Ζ	4	8
$D_{\rm c}({\rm gcm^{-1}})$	1.308	1.521
F(000)	912	3176
<i>T</i> (K)	293(2)	293(2)
$\mu(Mo K_{\alpha}) (mm^{-1})$	0.700	1.487
Scan mode	$\omega - 2 heta$	$\omega - 2\theta$
θ Range (°)	1.84; 24.97	2.16; 24.96
Limiting indices	$0 \leq h \leq 9, 0 \leq k \leq 15, -24 \leq l \leq 23$	$0 \leq h \leq 15, 0 \leq k \leq 22, 0 \leq l \leq 32$
Absorption correction	PSI-scan	PSI-scan
Reflections collected	4158	5996
Independent reflections $[I > 2.0\sigma (I)]$	3872	5996
Refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
Number of parameters refined	271	436
Final <i>R</i> indices $[I > 2.0\sigma (I)]$	R_1 , 0.0485; wR_2 , 0.1427	R_1 , 0.0944; wR_2 , 0.1910
R indices (all data)	R_1 , 0.1059; wR_2 , 0.1690	R_1 , 0.3446; wR_2 , 0.3014
Goodness-of-fit	1.016	0.931
Largest difference peak and hole (e $Å^{-3}$)	0.228 and -0.221	0.546 and -0.552

Table 2

Selected bond distances (Å) and angles (°) for HL6

Bond distances			
H–N	0.85(0)	C(1)–C(15)	1.516(7)
N–C(3)	1.349(5)	C(2)–C(13)	1.473(8)
C(3)–C(4)	1.367(5)	C(3)–C(45)	1.493(5)
C(4)–C(5)	1.408(5)	C(5)-C(34)	1.482(5)
O-C(5)	1.250(4)	C(14)–N	1.443(8)
Bond angles			
N-C(3)-C(4)	121.2(3)	N-C(3)-C(45)	118.4(3)
C(3)–C(4)–H	117.9(3)	O-C(5)-C(4)	123.0(3)
C(3)–C(4)–C(5)	124.2(3)	O-C(5)-C(34)	119.0(3)
C(5)–C(4)–H	117.9(3)	C(4)-C(5)-C(34)	117.9(3)
C(3)–N–C(14)	127.3(3)	$N\!\!-\!\!H\!\cdot\cdot\cdot\!O$	135
C(3)–N–H	116.3(3)		

to the unsubstituted cyclopentadienyl ring protons. For enaminones HL^1 , HL^2 and HL^3 , the methyl protons of the C(O)CHC(NHAr)CH₃ moiety show a singlet corresponding to 3H at δ 1.73–2.15 ppm. The methyl protons of the NHAr moiety also show a singlet corresponding to 3H and 6H for HL^2 and HL^5 and for HL^3 and HL^6 at δ 2.21–2.48 ppm, respectively. For each ligand, the vinylic proton as a singlet appears at δ 5.54– 5.70 ppm, and the relative integrated intensity ratio of this peak to other peaks shows that there is only one H atom bonded to the α -C atom in the C(O)C $_{\alpha}$ HC(N-HAr)R moiety. The aromatic protons of the ligands

Table 3							
Selected	bond	distances	(Å)	and	angles	(°)	for

Bond distances			
Cu-O(1)	1.92(1)	Cu-O(2)	1.89(1)
Cu-N(1)	1.95(1)	Cu-N(2)	1.99(1)
N(1)–C(2)	1.28(2)	N(2)–C(6)	1.31(2)
O(1)–C(4)	1.31(1)	O(2)–C(8)	1.31(2)
N(1)–C(14)	1.45(2)	N(2)–C(26)	1.42(2)
Bond angles			
O(1)-Cu-O(2)	154.1(5)	C(2)–N(1)–Cu	124.9(1)
O(1)–Cu–N(1)	92.1(5)	C(2)-N(1)-C(14)	117.4(1)
O(1)–Cu–N(2)	93.1(5)	C(14)–N(1)–Cu	117.5(1)
O(2)–Cu–N(1)	91.6(5)	C(6)–N(2)–Cu	123.1(1)
O(2)-Cu-N(2)	94.1(5)	C(6)-N(2)-C(26)	118.4(1)
N(1)-Cu-N(2)	155.5(5)	C(26)–N(2)–Cu	118.4(1)

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exhibit multiplets corresponding to 5H, 4H and 3H for HL^1 , HL^2 and HL^3 and 10H, 9H and 8H for HL^4 , HL^5 and HL^6 at δ 6.40–7.44 ppm, respectively. The spectra of all ligands display a singlet signal at δ 12.03–12.64 ppm, which is assigned to the enamino NH and disappears in the presence of D₂O. The downfield position of this signal may mainly arise from the intramolecular hydrogen bonding as shown in Scheme 1. Obviously, the above evidence is in agreement with the proposed structure of the ligands and also supported by the crystal structure of enaminone HL^6 [2a,3c].



$$2HL + Cu(OAc)_2 \xrightarrow{\text{Ethanol}} L_2Cu + 2HOAc$$
$$(L = L^1(I), L^2(II), L^3(III), L^4(IV), L^5(V))$$

Scheme 2. Syntheses of complexes.

3.3. Crystal structure

3.3.1. Crystal structure of HL⁶

As mentioned above, enaminones with the general formula [R'C(O)CHC(NHAr)R] may have the following four isomers: cis-s-cis, cis-s-trans, trans-s-cis and trans-strans in which cis and trans refer to two possible geometric arrangements for the carbon-carbon double bond and s-cis and s-trans to both isomerisms about the carbon-carbon single bond between the carbon-carbon and carbon-oxygen double bonds [2a]. Owing to very few X-ray diffraction studies, so far the structure of enaminones [R'C(O)CHC(NHAr)R] has resulted in inconsistencies and remains uncertain [2b,4]. Therefore, a single crystal X-ray analysis on HL⁶ was carried out to determine the structure of the new enaminones. The molecular structure of HL⁶ together with the atomic numbering is shown in Fig. 1. As seen from Fig. 1, HL⁶ in the solid state belongs to the cis-s-cis isomer. All atoms in the skeleton O = C - C = C - N can be regarded as sp^2 hybridized. As shown by the comparison of the C = O, C-C, C = C and C-N distances (Table 2) with the corresponding pure double or single bond distances

 $C(sp^2) = O \approx 1.20, C(sp^2) - C(sp^2) \approx 1.48, C(sp^2) = C(sp^2)$ \approx 1.33 and C(sp²)-N (sp²) \approx 1.44 Å, HL⁶ exhibits partial delocalization of the O = C - C = C - N system. That the $H \cdots O$ distance of 1.971 Å is significantly shorter than the sum of the van der walls radii (2.60 A) indicates the existence of intramolecular hydrogen bonding; this is also in accordance with spectroscopic data. The plane of the skeleton and the plane of the substituted cyclopentadienyl ring only form a dihedral angle of 13.6°, whereas the skeleton with the N-benzene ring and C-benzene ring makes two angles of 74.4 and 116.9° to avoid the steric repulsions. Therefore, in the solid state, neither the N-benzene ring nor the C-benzene ring is involved in the conjugation of the skeleton, whereas the substituted cyclopentadienyl ring may in part conjugate with the enaminonic system [3c,4a].

3.3.2. Crystal structure of complex I

In view of cis or trans isomerism of donor atoms and planar or tetrahedral coordination geometry of the central metal ion, as well as anti or svn arrangement of the ferrocenyl groups with respect to the plane with the central metal ion and donor atoms, four-coordinate copper(II) complexes may possess eight stereoisomers: planar-cis-anti, planar-cis-syn, planar-trans-anti, planartrans-syn, tetrahedral-cis-anti, tetrahedral-cis-syn, tetrahedral-trans-anti and tetrahedral-trans-syn [13,14]. Therefore, to further establish their structures and to provide more structural evidence for the new complexes, the crystal structure of complex I was determined. The molecular structure of the new copper complex I together with the atomic numbering is shown in Fig. 2. The metal atom displays a tetrahedral coordination geometry surrounded by two nitrogen atoms and two oxygen atoms of two deprotonated ligands (L-), so complex I exists only in the tetrahedral-trans-syn form, which is further supported by the above-described TLC. More interestingly, against usual expectation, both



Fig. 1. Molecular structure of enaminone HL^6 together with the atomic numbering. Hydrogen atoms are omitted for clarity.



Fig. 2. Molecular structure of complex I together with the atomic numbering. Hydrogen atoms and water molecules are omitted for clarity.

ferrocenyl groups in complex I are syn to each other. In view of the Fe $\cdot\cdot\cdot$ Fe distance of 10.502 Å, it may be concluded that one ferrocenyl group in complex I does not interact sterically with the other and therefore the syn isomer can be isolated, whereas the corresponding anti-isomer cannot be found. As expected, both six-membered chelate rings are planar. Angles O(1)-Cu-N(1) and O(2)-Cu-N(2), which are 92.1(5) and 94.1(5)°, are slightly larger than the corresponding values observed in related structures [15,16]. Values of angles O(1)-Cu-O(2) and N(1)-Cu-N(2) are 154.1(5) and $155.5(5)^{\circ}$, therefore indicating that the coordination geometry about the copper ion is tetrahedral as mentioned above. The bonds between the copper atom and the donor sites of the deprotonated ligand are within the range of values normally found for these bonds [15,16]. Interestingly, the Cu–O distances (Cu–O(1) = 1.92(1); Cu-O(2) = 1.89(1) A) are significantly different from each other whereas the Cu-N distances (Cu-N(1) = 1.95(1); Cu-N(2) = 1.99(1) Å) are similar. The structural features of two L^- ions (Table 3) are as follows. One exhibits N(1)–C(2), C(2)–C(3), C(3)–C(4) and O(1)-C(4) bond distances of 1.28(2), 1.42(2), 1.35(2) and 1.31(2) A, and the other shows N(2)–C(6), C(6)–C(7), C (7)-C(8) and O(2)-C(8) bond distances of 1.31(2), 1.42(2), 1.36(2) and 1.31(2) A whereas the corresponding bond distances of HL⁶ are 1.349(5), 1.367(5), 1.408(5) and 1.250(4) A. These suggest that the O = C - C = C - Nsystem of the complex has more delocalization than that of the corresponding ligand [16]. It should be pointed out that the water molecules in complex I are noncoordinate and disordered.

3.4. IR spectra

The important IR data of the enaminones and the complexes are given in Section 2. The band at ≈ 3080 cm⁻¹ in the spectrum of each ligand is due to v(NH) and does not occur in that of the corresponding complex. This suggests that the enaminones are bonded to copper ions in the monoanionic form. Moreover, the strong bands assignable to stretching vibrations of the skeleton C=O and C=C groups, which are observed at 1585–1603 and 1552–1567 cm⁻¹ in the ligands, are all redshifted to the region 1550–1580 and 1510–1513 cm⁻¹ in the complexes [3c,7a]. This is because the complexes possess resonance forms as shown in Fig. 3, which lead to a decrease in double bond character of the C=O and C=C groups [17]. As expected, the spectra of complexes I, IV and V display a broad and weak band at ≈ 3430



Fig. 3. Resonance forms of copper complexes.

 cm^{-1} due to the presence of v(OH) of lattice water molecules. Further, this has been confirmed by another band appearing at about 600 cm⁻¹ [18,19]. Also this is consistent with the above-described X-ray crystal structure determination and elemental analyses data.

3.5. UV spectra

The UV spectral data of the enaminones and the complexes are listed in Section 2. In the UV spectra, complexes I, II and III show three maxima at \approx 275, 350 and 450 nm while for complexes IV and V each exhibits one maxima at \approx 378 nm. The shortest wavelength absorption which is due to the B-band of cyclopentadienyl or benzene rings, displays a red shift compared with the corresponding ligand [20]. Unlike other ligands, only HL¹ exhibits the respective B-band for the cyclopentadienyl ring and benzene ring. On the other hand, the longer wavelength band in the region 350-379 nm may be attributed to the $(\pi \rightarrow \pi^*)$ transition (viz. K-band) while the corresponding absorption in each ligand is observed in the region 328-369 nm. Therefore, compared with those absorptions of the corresponding ligands, the K-bands of all the complexes also show red shifts. Because deprotonated ligands bonded to the central metal ions strengthen the conjugative effect of the skeleton as shown in Fig. 3, red shifts of K-bands in the complexes are observed, whereas slightly decreased bonding of the cyclopentadienyl groups of the complexes results in a bathochromic shift of the B-band of the cyclopentadienyl group, which is also supported by the X-ray crystallography of enaminone HL⁶ and complex I [20,21]. Furthermore, unlike the corresponding ligands, complexes I, II and III exhibit an intense absorption band in the region 450-447 nm which may be assignable to a ligand-to-metal charge transfer transition [22]. However for complexes IV and V no charge transfer transitions are observed. Finally, because weak d-d transtions in ferrocene-containing complexes are obscured by much more intense UV transitions from a different nature, the ligand field absorptions in these complexes cannot be resolved.

4. Conclusion

Reaction of the ferrocene-containing β -diketone [C₅H₅FeC₅H₄C(O)CH₂C(O)R] (1, R = CH₃; 2, R = C₆ H₅) and the corresponding aniline [H₂NAr] (Ar = Ph, 2-CH₃C₆H₄, 2,6-(CH₃)₂C₆H₃) in the presence of a catalytic amount of *p*-toluenesulfonic acid yields a series of *cis*-s-*cis* enaminones [C₅H₅FeC₅H₄C(O)CH = C(NH Ar)R] (HL¹-HL⁶). Reaction of enaminones HL¹-HL⁵ and copper acetate affords tetrahedral-*trans*-syn complexes I–V in which each of the enaminones coordinates to the copper ion as a monoanionic bidentate ligand via

carbonyl oxygen and enamine nitrogen atoms after deprotonation.

5. Supplementary material

Full crystallographic data (CCDC No. 200938 for enaminone HL⁶ and CCDC No. 207417 for complex I) have been deposited at the Cambridge Crystallographic Database Centre and are available on request from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; Email:deposit@ccdc. cam.ac.uk or http://www.ccdc.cam.ac.uk).

Acknowledgements

We thank the National Nature Science Foundation of China (No. 20175023) and Yangzhou University (No. D0009107) for financial support of this work.

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