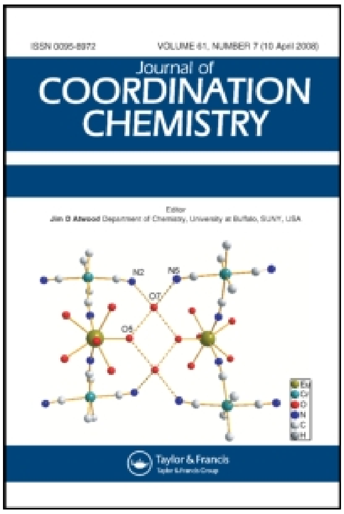

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Syntheses and structures of copper complexes of tetradentate enaminones derived from condensation of benzoylacetone and ferrocenoylacetone with 1,2-*bis*(2-aminophenoxy)ethane

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Reaction of 1,2-*bis*(2-aminophenoxy)ethane with benzoylacetone and ferrocenoylacetone yields tetradentate enaminones H_2L^1 and H_2L^2, respectively. Reaction of copper acetate with two enaminones affords the corresponding complexes **1** and **2**, which are formulated as [L^1Cu] and [L^2Cu], respectively. The structures of H_2L^1, H_2L^2 and **1** have been determined by single-crystal X-ray crystallography. Enaminone H_2L^1 crystallizes with $Z = 4$ in space group $C2/c$, the molecule of which lies on a C_2 axis. Enaminone H_2L^2 crystallizes with $Z = 2$ in space group $P2_1/c$, the molecule of which possesses a symmetric center. For complex **1**, which crystallizes in space group $P\bar{1}$, H_2L^1 is a bianionic tetradentate donor via two carbonyl oxygens and two deprotonated enamine nitrogens; the coordination geometry of copper(II) is a distorted tetrahedron.

Keywords: β-Diketone; Enaminone; Complex; Copper; X-ray crystallography

1. Introduction

Multidentate ligands with varying combinations of donor atoms and charges have become increasingly popular for bonding transition metals, lanthanides, and main group elements [1–3]. Complexes of enaminones have attracted attention because Group IV metal complexes are alternatives to metallocene catalysts, and anions generated from enaminones are isoelectronic alternatives to cyclopentadienyl-based anions [4–8]. Enaminones are easily synthesized from inexpensive and readily available starting materials. More importantly, through an appropriate choice of primary amine and β-diketone used in their syntheses, the steric and electronic properties of enaminones can be tuned and chirality and further functionalization readily introduced [9–11]. These enaminones are versatile synthetic intermediates that combine the nucleophilicity of enamines with the electrophilicity of enones and have been extensively used for preparation of a variety of heterocyclic systems including some natural products and analogues [12, 13]. As part of an ongoing investigation of the chemistry of enaminones, the title compounds have been synthesized and structurally characterized [14–20].

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2. Experimental

2.1. *Reagents and general procedures*

All chemicals were of reagent grade. Air-sensitive reactions were carried out under dinitrogen, but subsequent work-up was in air. Ferrocenoylacetone and benzoylacetone were synthesized by acylation of acetylferrocene and acetophenone using ethyl acetate in THF in the presence of sodium ethoxide [14]. Progress of reactions was monitored by TLC (silica gel H). ^{1}H NMR spectra were carried out on a Bruker Avance 600 spectrometer using TMS as an external standard in $CDCl_3$. IR spectra were recorded on a Bruker Tensor 27 spectrometer as KBr disks in the range 400–4000 cm^{-1}. UV spectra were measured with a Shimadzu UV-2550 spectrometer in DMF. Analyses for C, H, and N were performed on an Elementa Vario EL III instrument. Melting points were measured on a Yanagimoto apparatus and are uncorrected.

2.2. *Syntheses of tetradentate enaminones H_2L^1 and H_2L^2*

A 25 mL toluene solution of benzoylacetone (0.649 g, 4 mmol) and 1,2-*bis*(2-aminophenoxy)ethane (0.485 g, 2 mmol) in the presence of a catalytic amount of *p*-toluenesulfonic acid (0.01 g) was refluxed for 42 h. After removal of the solvent under reduced pressure, the crude product was purified by column chromatography on silica gel (200–300 mesh) using diethyl ether and petroleum ether (v/v, 1 : 1) as eluent to afford 1.96 g (73%) of enaminone HL^1 as a yellow solid. M.p. 135–135.8°C. Anal. Calcd for $C_{34}H_{32}N_2O_4$ (%): C, 76.66; H, 6.06; N, 5.26. Found: C, 76.44; H, 6.08; N, 4.97. IR (KBr disk): ν(NH) 3042 (m), ν(C=O) and ν(C=C) 1609 (vs) and 1542 (vs) cm^{-1}. UV (nm, in DMF): λ_{max} ($\varepsilon \times 10^4$, in $dm^3\,mol^{-1}\,cm^{-1}$) 271 (B-band) (0.64), 364 (K-band) (2.16) nm. ^{1}H NMR ($CDCl_3$): δ 2.10 (s, 6H, $2CH_3$), 4.496 (s, 4H, $2OCH_2$), 5.87 (s, 2H, 2CH), 6.93–6.96, 7.10–7.18, 7.40–7.47, 7.88–7.89 [t, m, m, d, 2H, 6H, 6H, 4H, $2(C_6H_4/C_6H_5)$], 13.59 (s, 2H, 2NH) ppm.

Similar reaction of ferrocenoylacetone (0.540 g, 2 mmol) and 1,2-*bis*(2-aminophenoxy)ethane (0.242 g, 1 mmol) in 25 mL of toluene for 18 h afforded 0.485 g (65%) of enaminone H_2L^2 as a red solid. M.p. 207.8–208.0°C. Anal. Calcd for $C_{42}H_{40}N_2O_4Fe_2$ (%): C, 67.36; H, 5.39; N, 3.74. Found: C, 67.22; H, 5.46; N, 3.93. IR (KBr disk): ν(NH) 3082 (w), ν(C=O) and ν(C=C) 1609 (vs) and 1551 (vs) cm^{-1}. UV (nm, in DMF): λ_{max} ($\varepsilon \times 10^4$, in $dm^3\,mol^{-1}\,cm^{-1}$) 269 (B-band) (0.45), 330 (K-band) (1.36), 448 (CT-band) (0.065) nm. ^{1}H NMR ($CDCl_3$): δ 2.10 (s, 6H, $2CH_3$), 4.10 (s, 10H, $2C_5H_5$), 4.32 (s, 4H, $2(H^3, H^4)$ of C_5H_4 rings), 4.33 (s, 4H, $2OCH_2$), 4.70 (s, 4H, $2(H^2, H^5)$ of C_5H_4 rings), 5.39 (s, 2H, 2CH), 6.90–7.12 (m, 8H, $2C_6H_4$), 12.41 (s, 2H, 2NH) ppm.

2.3. *Syntheses of complexes 1 and 2*

A solution of $Cu(OAc)_2 \cdot H_2O$ (0.080 g, 0.4 mmol) and H_2L^1 (0.213 g, 0.4 mmol) in 15 mL of absolute ethanol was stirred for 6 h at room temperature. The mixture was filtered to afford the brown crude product. The resulting solid was recrystallized from dichloromethane and petroleum ether (60–90 °C) to give 0.216 g (91%) of **1** as brown crystals. D.p. 176.2–176.8°C. Anal. Calcd for $C_{34}H_{30}N_2O_4Cu$ (%): C, 68.73; H, 5.09; N, 4.71. Found: C, 68.50; H, 4.74; N, 4.41. IR (KBr disk): ν(C=O) 1571 (vs), ν(C=C) 1504 (vs) cm^{-1}. UV (nm, in DMF): λ_{max} ($\varepsilon \times 10^4$, in $dm^3\,mol^{-1}\,cm^{-1}$) 292 (B-band) (0.91), 357 (1.55) (K-band) nm.

Similar reaction of $Cu(OAc)_2{\cdot}H_2O$ (0.060 g, 0.3 mmol) and H_2L^2 (0.225 g, 0.3 mmol) in 15 mL of absolute ethanol afforded 0.158 g (65%) of **2** as brown crystals. M.p. 101.5–101.9°C. Anal. Calcd for $C_{42}H_{38}Fe_2N_2O_4Cu$ (%): C, 62.28; H, 4.73; N, 3.46. Found: C, 62.03; H, 4.61; N, 3.56. IR (KBr disk): ν(C=O) 1588 (s), ν(C=C) 1506 (vs) cm^{-1}. UV (nm, in DMF): λ_{max} ($\varepsilon \times 10^4$, in $dm^3\,mol^{-1}\,cm^{-1}$) 288 (B-band) (5.69), 348 (3.87) (K-band), 451 (0.12) (CT-band) nm.

2.4. *Crystal structure determinations*

Single crystals suitable for X-ray diffraction were obtained by slow evaporation from dichloromethane and petroleum ether solutions of H_2L^1, H_2L^2 and **1**. X-ray data of the three compounds were collected on an Enraf-Nonius CAD4 diffractometer at 295 K using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods and subsequently refined on F^2 using full-matrix least-squares methods, all non-hydrogen atoms were refined anisotropically, and hydrogen atoms were located at calculated positions [21, 22]. A summary of the data collection and structure refinement parameters of HL^1, H_2L^2 and **1** is given in table 1. Plots of H_2L^1, H_2L^2 and **1** are drawn using PLATON software [23].

3. Results and discussion

3.1. *Syntheses of tetradentate enaminones and copper complexes*

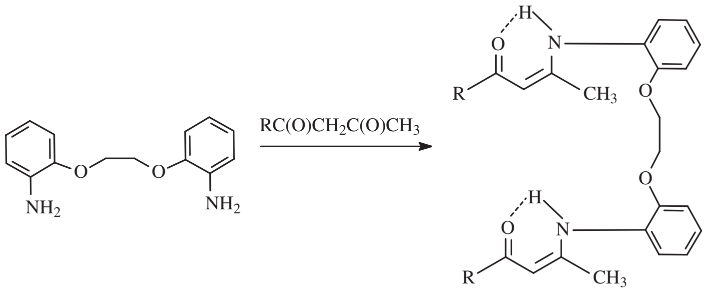
1,2-*Bis*(2-aminophenoxy)ethane reacts with benzoylacetone and ferrocenoylacetone to afford tetradentate enaminones H_2L^1 and H_2L^2, as shown in equation (1). Reactions of copper acetate with H_2L^1 and H_2L^2 give the corresponding complexes **1** and **2**, formulated as [L^1Cu] and [L^2Cu], respectively [equation (2)]. Structures have been unambiguously determined by single-crystal X-ray crystallography for H_2L^1, H_2L^2 and **1**.

3.2. *Crystal structures*

3.2.1. Crystal structures of H_2L^1 and H_2L^2. The molecular structures of enaminones H_2L^1 and H_2L^2 are shown in figures 1 and 2. Selected geometric parameters for H_2L^1 and H_2L^2 are listed in tables 2 and 3. H_2L^1 lies on a two-fold rotation axis and H_2L^2 possesses a symmetric center. As noted previously, the O=C–C=C–N moiety is planar and the bond lengths indicate electron delocalization [14, 24]. However, H_2L^1 and H_2L^2 show different conformations. The O=C–C=C–N plane is twisted with respect to the monosubstituted benzene or substituted cyclopentadiene ring and the disubstituted benzene ring by 16.8(2)° and 35.5(1)° for H_2L^1 and 9.6(3)° and 46.6(3)° for H_2L^2.

Table 1. Summary of the data collection and structure refinement parameters of H_2L^1, H_2L^2, and **1**.

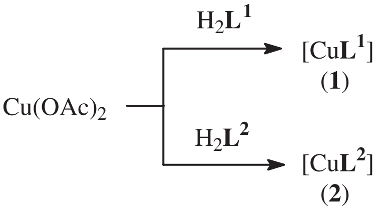
Compound	H_2L^1	H_2L^2	**1**
Formula	$C_{34}H_{32}N_2O_4$	$C_{42}H_{40}Fe_2N_2O_4$	$C_{34}H_{30}CuN_2O_4$
Formula weight	532.62	748.46	594.15
Crystal size (mm)	$0.17 \times 0.17 \times 0.14$	$0.22 \times 0.15 \times 0.13$	$0.21 \times 0.17 \times 0.12$
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$C2/c$	$P2_1/c$	$P\bar{1}$
Unit cell dimensions (°, Å)			
a	20.7943(11)	14.329(2)	9.759(3)
b	14.5650(8)	10.938(2)	10.592(2)
c	9.2456(14)	11.351(2)	14.791(1)
α			95.23(2)
β	93.371(6)	100.57(2)	90.10(1)
γ			110.15(2)
V (Å^3)	2795.4(5)	1748.9(5)	1428.5(6)
Z	4	2	2
D_c (g cm^{-1})	1.266	1.421	1.381
F (000)	1128	780	618
T(K)	295	295	295
μ (Mo-Kα)(mm^{-1})	0.083	0.876	0.806
Scan mode	$\omega - 2\theta$	$\omega - 2\theta$	$\omega - 2\theta$
θ Range (°)	1.71–25.97	1.45–25.99	1.38–25.97
Limiting indices	$0 \le h \le 25$, $0 \le k \le 17$, $-11 \le l \le 11$	$-17 \le h \le 17$, $-13 \le k \le 0$, $0 \le l \le 13$	$0 \le h \le 12$, $-13 \le k \le 12$, $-18 \le l \le 18$
Absorption correction	PSI-scan	PSI-scan	PSI-scan
Reflections collected	2803	3615	5914
Independent reflections	2729 [$R_{\text{int}} = 0.047$]	3430 [$R_{\text{int}} = 0.036$]	5565 [$R_{\text{int}} = 0.048$]
No. of parameters refined	186	227	372
Final R indices [$I > 2.0\sigma(I)$]	R, 0.0621; wR, 0.1138	R, 0.0663; wR, 0.1106	R, 0.0873; wR, 0.1844
R indices (all data)	R, 0.1451; wR, 0.1436	R, 0.1447; wR, 0.1355	R, 0.1537; wR, 0.2124
Goodness of Fit	1.01	1.02	1.09
Max peak and hole (e Å^{-3})	0.17 and −0.22	0.32 and −0.32	0.58 and −0.66



R = Ph, $H_2\mathbf{L}^1$; R = Fc, $H_2\mathbf{L}^2$

Equation 1. Syntheses of tetradentate enaminones.

Consistent with the large dihedral angles between the O=C–C=C–N plane and substituted cyclopentadienyl ring, the C6–C7 and C10–C11 bonds linking the O=C–C=C–N moiety and the monosubstituted benzene or the substituted cyclopentadienyl ring are typical of a single bond (Csp2–Csp2), suggesting that the monosubstituted



Equation 2. Syntheses of copper complexes.

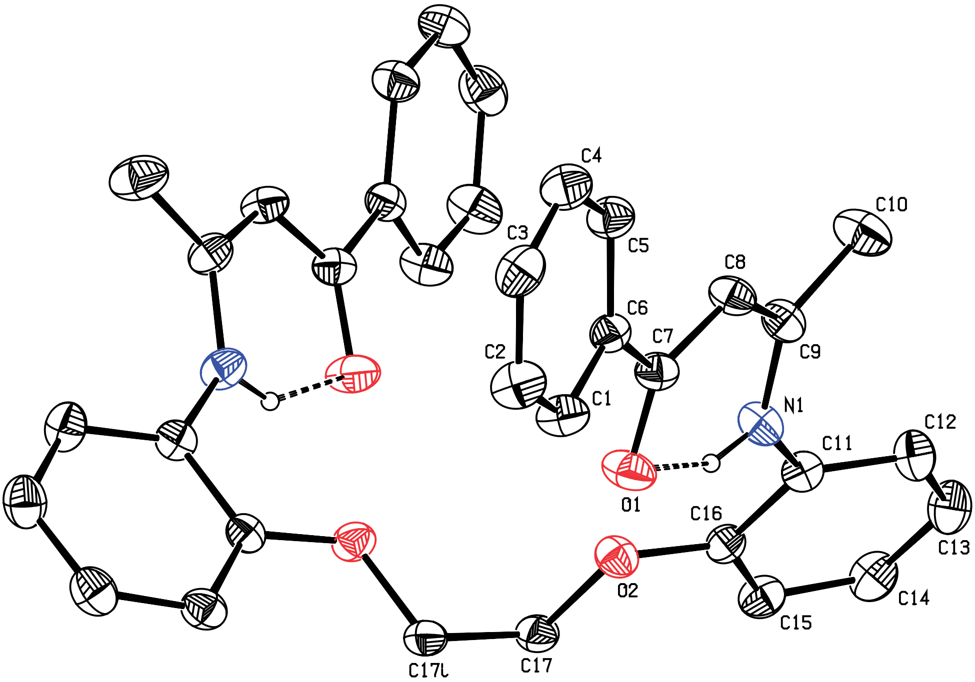


Figure 1. ORTEP plot of H$_2$L^1 showing atom labeling; thermal ellipsoids are drawn at the 30% probability ellipsoids. Symmetry code: (i) $1-x$, y, $1/2-z$. The intramolecular hydrogen bond is shown as a dashed line.

benzene or substituted cyclopentadienyl ring is not involved in conjugation of the O=C–C=C–N moiety.

Although both enaminones have strong [N–H $\cdots$ O=C] intramolecular hydrogen bonds, their packing modes generated from the weak interactions are markedly different (figures 3 and 4). For H$_2$L^1, atom C17 in molecule at (x, y, z) is a hydrogen-bond donor via H17A to carbonyl atom O1 at (x, $1-y$, $-1/2+z$) and O1 at (x, y, z) acts as a hydrogen-bond acceptor; C17 at (x, $1-y$, $½+z$) is a hydrogen-bond donor, generating an infinite 1-D chain in the [001] direction (figure 3). For H$_2$L^2, weak C–H $\cdots$ π(Cp) hydrogen bonds are present in which C16 at (x, y, z) is a hydrogen-bond donor via H16 to the C1–C5 ring at (x, $-1+y, z$), resulting in an infinite 1-D chain in the [010] direction (figure 4).

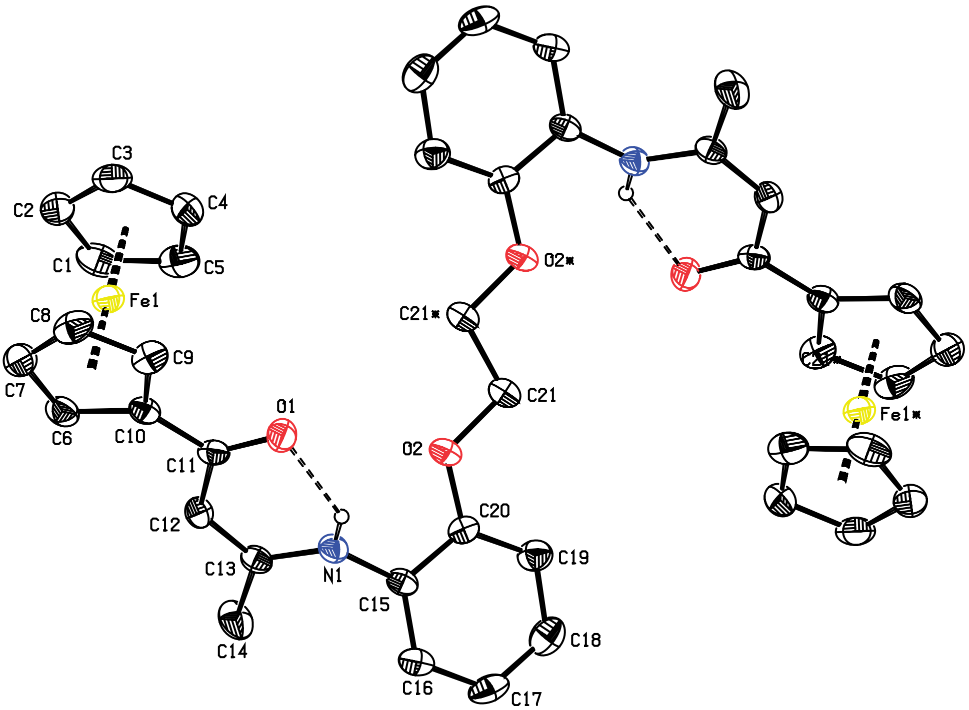


Figure 2. ORTEP plot of H_2L^2 showing atom labeling; thermal ellipsoids are drawn at the 30% probability ellipsoids. Symmetry code: (*) $1-x$, $1-y$, $1-z$. The intramolecular hydrogen bond is shown as a dashed line.

Table 2. Selected geometric parameters (Å, °) for H_2L^1.

O1–C7	1.244(3)	C8–C9	1.377(4)
C6–C7	1.500(4)	C9–N1	1.345(4)
C7–C8	1.416(4)	C11–N1	1.414(3)
C17···O1[a]	3.390(3)	N1···O1	2.647(3)
H17A···O1[a]	2.48	H1N···O1	1.95(3)
O1–C7–C6	118.4(3)	N1–C9–C8	119.9(3)
O1–C7–C8	122.2(3)	N1–C9–C10	120.6(3)
C6–C7–C8	119.3(3)	C8–C9–C10	119.5(3)
C7–C8–C9	125.3(3)	C9–N1–C11	131.1(3)
C17–H17A···O1[a]	156	N1–H1N···O1	141(3)

Note: [a]Symmetry code: x, $1-y$, $-1/2+z$.

3.2.2. Crystal structure of 1. The molecular structure of **1** is shown in figure 5 and selected geometric parameters are listed in table 4. In **1**, H_2L^1 is a dianionic tetradentate ligand after deprotonation of two enamine nitrogens, namely an N2O2 donor. Against expectation, copper(II) ion is not coplanar with the O=C–C=C–N plane, with distances of 0.2461(9) and 0.3484(9) Å, for planes O1–N1–C7–C8–C9 and O3–N2–C26–C27–C28, respectively. The OCH_2CH_2O bridge has a gauche conformation, with torsion angle of −67.2(8)° for O2–C17–C18–O4. The angles 149.8(2)°, 93.0(2)°, 160.6(3)° and 92.9(2)° of O1–Cu1–O3, O1–Cu1–N1, N1–Cu1–N2 and N2–Cu1–O3, respectively, indicate that the coordination geometry of copper(II) is

Table 3. Selected geometric parameters (Å, °) for H_2L^2.

O1–C11	1.246(5)	C13–N1	1.342(6)
C10–C11	1.481(7)	C13–C14	1.483(6)
C11–C12	1.424(7)	C15–N1	1.415(6)
C12–C13	1.378(6)	N1· · ·O1	2.650(5)
C16· · ·Cg1[a]	3.455	N1–H1N	0.86
H16· · ·Cg1[a]	2.762	H1N· · ·O1	1.95
O1–C11–C10	118.9 (5)	N1–C13–C12	119.6(5)
O1–C11–C12	122.9 (5)	N1–C13–C14	119.2(4)
C10–C11–C12	118.2 (5)	C12–C13–C14	121.1(5)
C11–C12–C13	124.9 (5)	C13–N1–C15	129.3(4)
C16–H16· · ·Cg1[a]	132	N1–H1N· · ·O1	137

Notes: Cg1 is the centroid of the C1–C5 ring.
[a] Symmetry code: x, $-1+y$, z.

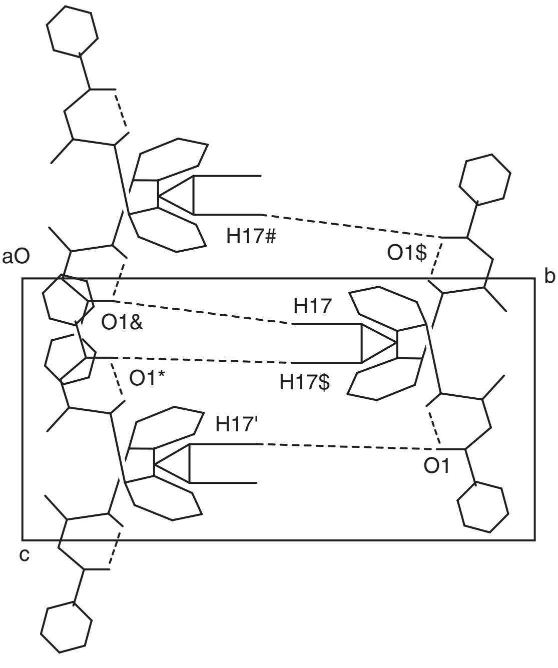


Figure 3. Packing diagram of H_2L^1 showing formation of an infinite chain in the [001] direction. Dashed lines indicate hydrogen bonds. For clarity, H atoms not involved in the motif have been omitted. Atoms marked with an ampersand (&), hash (#), dollar sign ($), asterisk (*) or prime (′) are at the symmetry positions $(x, 1-y, -1/2+z)$, $(1-x, 1-y, -z)$, $(1-x, y, 1/2-z)$, $(1-x, 1-y, 1-z)$ and $(x, 1-y, ½ + z)$, respectively.

tetrahedrally-distorted, due to weak interactions from the Cu1 to O2 and O4 at 3.292(5) and 3.173(6) Å, respectively. Therefore, the measured N–Cu–N and O–Cu–O angles are considerably larger than the corresponding values observed in related structures [16, 25–28]. Bond lengths of Cu1–O1, Cu1–O3 and Cu1–N1, Cu1–N2 are 1.898(5), 1.903(5) and 1.950(5), 1.966(5) Å and are considerably shorter than those reported for N,N'-ethylenebis(acetylacetoneiminato)copper (mean 1.94 and 1.98 Å) [25]. Interestingly, Cu–O bonds are significantly shorter than those in $[C_5H_5FeC_5H_4C(O)CH{=}C(CH_3)NCH_2]_2Cu$ [mean 1.924(6) for the anti isomer and

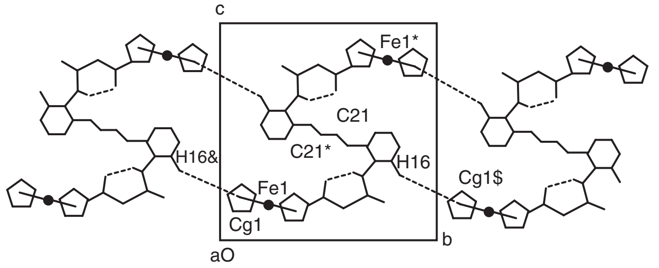


Figure 4. Packing diagram of H_2L^2 showing the formation of an infinite chain via C–H $\cdots$ π(Cp) hydrogen bonds in the [010] direction. Dashed lines indicate hydrogen bonds. For clarity, H atoms not involved in the motif have been omitted. Atoms marked with an asterisk (*), ampersand (&) or dollar sign ($) are at the symmetry positions ($1-x$, $1-y$, $1-z$), (x, $-1+y$, z) and (x, $1+y$, z), respectively.

1.913(6) Å for the syn isomer]. However, Cu–N bonds are significantly longer than those in $[C_5H_5FeC_5H_4C(O)CH{=}C(CH_3)NCH_2]_2Cu$ [1.927(8) Å for the anti isomer and 1.924(8) Å for the syn isomer] [16, 29, 30]. Like H_2L^1, bond lengths of the O=C–C=C–N indicate delocalization of bonding electron density. The dihedral angles between the O=C–C=C–N plane and monosubstituted benzene rings, C1–C5 and C29–C34, are 23.7(4)° and 4.1(4)°, respectively. Furthermore, the C6–C7 and C28–C29 bonds of 1.490(10) and 1.491(10) Å linking the O=C–C=C–N moiety and the monosubstituted benzene ring are typical of a single bond (Csp2–Csp2), suggesting that the benzene ring is not involved in conjugation of the O=C–C=C–N moiety.

Although **1** is chiral, it crystallizes in the achiral space group listed in table 4, crystallizing as a racemate in the unit cell.

3.3. *^{1}H NMR spectra*

The ^{1}H NMR spectrum of H_2L^1 reveals that it exists entirely in the bis(ketoenamine) form, shown in equation (1) [14, 31–33]. Protons of $C(O)CH{=}CCH_3$ show singlets at δ 5.87 and 2.10 ppm, respectively. The OCH_2 exhibits a singlet at δ 4.496 ppm. The monosubstituted and disubstituted phenyl groups display one triplet at δ 6.93–6.96 ppm, two multiplets at 7.10–7.18 and 7.40–7.47 ppm and one doublet at δ 7.88–7.89 ppm. The NH is a singlet at δ 13.59 ppm and disappears in the presence of D_2O. The very downfield position of this singlet results from intramolecular hydrogen bonding. In the spectrum of H_2L^2, the ferrocenyl group is three singlets at δ 4.10, 4.32 and 4.70 ppm. Protons of the $C(O)CH{=}CCH_3$ moiety show singlets at δ 5.39 and 2.10 ppm. The OCH_2 is a singlet at δ 4.33 ppm and the NH at δ 12.41 ppm, disappearing in D_2O.

3.4. *IR spectra*

IR spectra of **1** and **2** display significant changes compared with H_2L^1 and H_2L^2. Bands at 3042–3082 cm^{-1} in H_2L^1 and H_2L^2 due to ν(NH) do not appear in **1** and **2**. Furthermore, strong bands assignable to stretching vibrations of skeleton O=C and C=C groups, at 1609, 1542, and 1609, 1551 cm^{-1} in H_2L^1 and H_2L^2, respectively, shift to 1571, 1504 and 1588, 1506 cm^{-1} [14–18]. Therefore, H_2L^1 and H_2L^2 are dianionic N_2O_2 tetradentate ligands coordinated to copper(II) via two carbonyl oxygens and two deprotonated enamine nitrogens, in agreement with the crystal structure of **1**.

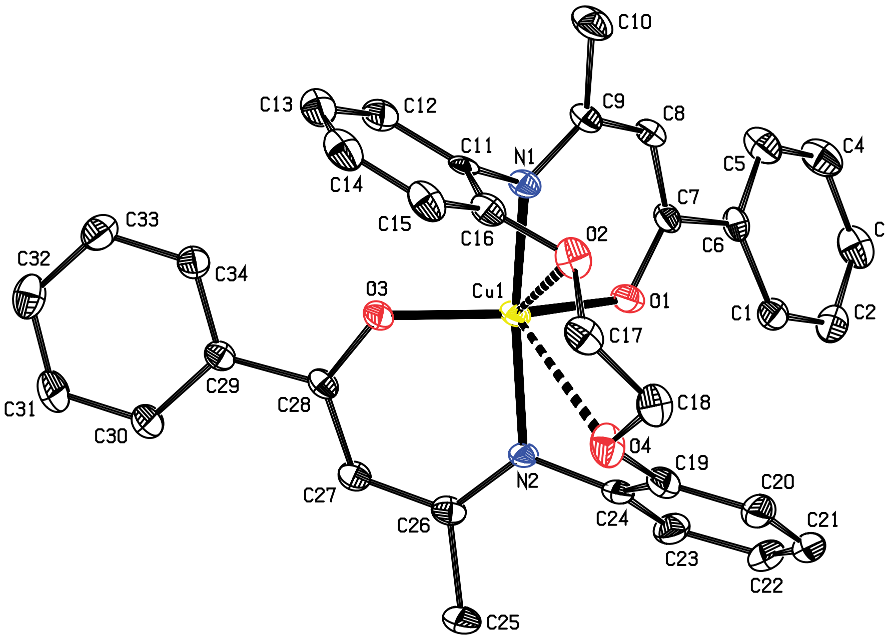


Figure 5. ORTEP plot of **1** showing atom labeling; thermal ellipsoids are drawn at the 30% probability ellipsoids. Dashed lines indicate weak interactions from Cu1 to O2 and O4.

Table 4. Selected geometric parameters (Å, °) for **1**.

O1–C7	1.285(8)	C26–N2	1.310(9)
C6–C7	1.490(10)	C26–C27	1.397(10)
C7–C8	1.368(9)	C27–C28	1.376(9)
C8–C9	1.406(10)	C28–C29	1.491(10)
C9–N1	1.308(8)	Cu1–O1	1.898(5)
C9–C10	1.513(10)	Cu1–O3	1.903(5)
C11–N1	1.455(8)	Cu1–N1	1.950(5)
C24–N2	1.419(9)	Cu1–N2	1.966(5)
C25–C26	1.531(10)		
O1–C7–C6	114.2(6)	C26–C27–C28	126.6(7)
O1–C7–C8	124.1(7)	O3–C28–C27	123.7(7)
C6–C7–C8	121.7(6)	O3–C28–C29	114.3(6)
C7–C8–C9	126.6(6)	C27–C28–C29	122.0(6)
N1–C9–C8	122.5(6)	O1–Cu1–O3	149.8(2)
N1–C9-C10	119.9(7)	O1–Cu1–N1	93.0(2)
C8–C9–C10	117.6(6)	O3–Cu1–N1	92.9(2)
N2–C26–C27	123.6(7)	O1–Cu1–N2	91.3(2)
N2–C26–C25	120.0(7)	O3–Cu1–N2	92.9(2)
C25–C26–C27	116.4(6)	N1–Cu1–N2	160.6(2)

3.5. *UV spectra*

In UV spectra, H_2L^1 and **1** show maxima at ca. 271–292 and 357–364 nm, which are attributed to the B-band of the benzene ring and K-band. However, H_2L^2 and **2** display maxima at ca. 269–288, 330–348 and 448–451 nm due to the B-band of benzene and cyclopentadienyl rings, K-band and CT-band of the ferrocenyl group [14–18].

For **1** and **2**, the B-band is red shifted compared with H_2L^1 and H_2L^2, whereas the K-band exhibits a blue shift. For the CT-band, **2** shows a slight red shift.

4. Conclusion

Reaction of 1,2-*bis*(2-aminophenoxy)ethane with benzoylacetone and ferrocenoylacetone give tetradentate enaminones H_2L^1 and H_2L^2, respectively. Reaction of copper acetate with H_2L^1 and H_2L^2 gave the corresponding complexes **1** and **2**, formulated as [L^1Cu] and [L^2Cu], respectively. The crystal structures of H_2L^1, H_2L^2 and **1** have been determined by single-crystal X-ray crystallography. In **1**, the coordination geometry of the central metal is a distorted tetrahedron in which the ligand is a dianionic N_2O_2 donor via two carbonyl oxygens and two deprotonated enamine nitrogens.

Supplementary data

Full crystallographic data (CCDC No. 683404 for H_2L^1, CCDC No. 683405 for H_2L^2 and CCDC No. 683598 for **1**) 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).

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