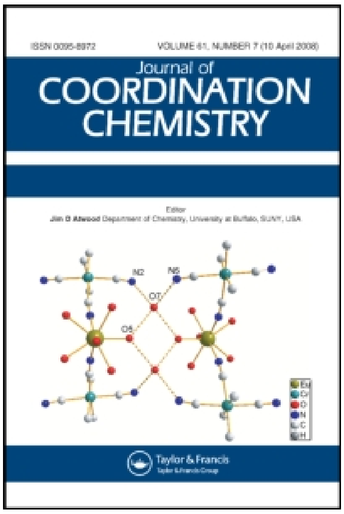

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Syntheses and crystal structures of a tridentate enaminone and its copper complex

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Syntheses and crystal structures of a tridentate enaminone and its copper complex

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Reaction of ferrocenoylacetone [$C_5H_5FeC_5H_4C(O)CH_2C(O)CH_3$] and 2-aminoethanol yields a new ferrocene-containing ligand (**H_2L**) that exists in the form of an enaminone formulated as [$C_5H_5FeC_5H_4C(O)CH{=}C(NHCH_2CH_2OH)CH_3$]. Reaction of the enaminone **H_2L** with copper acetate affords complex **1**. X-ray crystallography of **1** reveals that it has a tetrameric structure composed of four **CuL** subunits linked by bridging alkoxide oxygen atoms in which the enaminone acts as a dianionic tridentate ligand and each of the four copper atoms is in a distorted square-pyramidal coordination environment.

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

1. Introduction

Enaminones have attracted much interest recently not only because they can be used as good chelating ligands for transition metals but also because the anions generated from them offer potential isoelectronic alternatives to cyclopentadienyl-based anions and therefore their transition metal complexes can act as possible alternatives for olefin polymerization catalysts [1–3]. However, so far only a few organometallic enaminones have been studied [4–7]. We report here the syntheses and crystal structures of a new ferrocenyl enaminone and its copper complex.

2. Experimental

2.1. *Reagents and general procedures*

All chemicals used were of reagent grade. Ferrocenoylacetone [$C_5H_5FeC_5H_4C(O)CH_2C(O)CH_3$] was synthesized by acylation of acetylferrocene on the substituted

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cyclopentadienyl ring using ethyl acetate in THF in the presence of sodium ethoxide [4]. The progress of the reaction was monitored by TLC. The ^{1}H NMR spectrum was recorded with a Bruker Avance 300 spectrometer using TMS as external standard in $CDCl_3$. IR spectra were recorded on a Perkin-Elmer 402 instrument in the range of 400–4000 cm^{-1} using KBr disks. UV spectra were measured with a Shimadzu UV-240 spectrometer using a solution in DMF in the range of 200–800 nm. C, H and N analyses were performed on an Elementa Vario EL III instrument. Melting points were measured on a Yanagimoto apparatus and are uncorrected.

2.2. *Synthesis of enaminone*

A solution of ferrocenoylacetone (1.35 g, 5 mmol) and 2-aminoethanol (0.305 g, 5 mmol) in 20 mL of absolute ethanol was refluxed for 16 h. The solvent was evaporated under vacuum, and the residue was recrystallized from petroleum ether (60–90°C) to afford enaminone $\mathbf{H_2L}$ (1.466 g, 94%) as a red crystalline solid; m.p. 138°C. Anal. Calc. for $C_{16}H_{19}NFeO_2$(%): C, 61.36; H, 6.11; N, 4.47. Found: C, 61.75; H, 6.54; N, 4.12. IR (KBr disk, cm^{-1}): ν(C=C) 1529 (vs), ν(C=O) 1595 (vs), ν(NH) 3093 (m), ν(OH) 3270 (s). UV (nm, in DMF): λ_{max} ($\varepsilon \times 10^4$) 273 (0.52) (B-band), 339 (1.83) (K-band), 448 (0.07) (CT-band). ^{1}H NMR ($CDCl_3$): δ1.99 (s, 3H, CH_3), 3.41–3.46 (t, 2H, $J_{HH} = 5.4$ Hz, NCH_2), 3.79–3.82 (t, 2H, $J_{HH} = 5.4$ Hz, OCH_2), 4.14 (s, 5H, C_5H_5), 4.15 (s, 1H, OH), 4.34 (t, 2H, 2 (H^3, H^4) of C_5H_4 ring), 4.70 (t, 2H, 2 (H^2, H^5) of C_5H_4 ring), 5.25 (s, 1H, CH), 10.97 (s, 1H, NH).

2.3. *Synthesis of copper complex*

A solution of 0.25 mmol (78 mg) of the enaminone ligand $\mathbf{H_2L}$ in absolute ethanol (5 mL) was added dropwise to a stirred solution of 0.25 mmol (50 mg) of copper acetate monohydrate in the same solvent (10 mL). The mixture was stirred for 2 h at room temperature and then filtered to afford a yellow–green solid, which was recrystallized from CH_2Cl_2 and petroleum ether (60–90°C) to give complex **1** (84 mg, 90%) as dark green crystals; m.p. (dec.) 228–229°C (dry sample). Anal. Calc. for $C_{64}H_{68}N_4O_8Fe_4Cu_4$ (%): C, 51.29; H, 4.57; N, 3.74. Found: C, 51.42; H, 4.79; N, 3.51. IR (KBr disk, cm^{-1}): ν(C=C) 1499 (vs), ν(C=O) 1576 (m). UV (nm, in DMF): λ_{max} ($\varepsilon \times 10^4$) 261 (3.7) (B-band), 351(4.9) (K-band), 445 (0.036) (CT-band).

2.4. *Crystal structure determinations*

Single crystals of enaminone $\mathbf{H_2L}$ for X-ray analysis were obtained by slow evaporation of a solution of $\mathbf{H_2L}$ in CH_2Cl_2 and petroleum ether at *ca* 5°C. Single crystals of complex **1** for structure determination were grown by petroleum ether (60–90°C) diffusion into the CH_2Cl_2 and ethanol solution at *ca* 5°C. X-ray data were collected on a Bruker SMART CCD area detector diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 293 K. Intensity data were corrected using the multiscan method. 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 nonhydrogen atoms. Hydrogen atoms were placed in their calculated positions, assigned fixed isotropic thermal parameters and allowed to ride on their respective

Table 1. Crystallographic data for enaminone **H_2L** and complex **1**.

	H_2L	**1** $\cdot CH_2Cl_2 \cdot CH_3OH$*
Formula	$C_{16}H_{19}FeNO_2$	$C_{66}H_{74}Cl_2Fe_4N_4O_9Cu_4$
Formula weight	313.17	1615.75
Crystal size (mm)	0.20 × 0.16 × 0.10	0.18 × 0.16 × 0.12
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
Unit cell dimensions		
a (Å)	16.539(6)	14.02(2)
b (Å)	10.061(4)	14.58(2)
c (Å)	8.840(4)	19.37(2)
α (°)	90.00	97.36(2)
β (°)	100.405(6)	110.30(2)
γ (°)	90.00	107.84(2)
V (Å^3)	1447(1)	3411(7)
Z	4	2
D_c (g cm^{-1})	1.438	1.573
F(000)	656	1648
T (K)	293(2)	293(2)
μ (Mo Kα) (mm^{-1})	1.042	2.182
Scan mode	ω–2θ	ω–2θ
θ range (°)	1.25; 26.48	1.16; 26.91
limiting indices	$-20 \le h \le 20$ $-7 \le k \le 12$ $-11 \le l \le 10$	$-17 \le h \le 17$ $-18 \le k \le 18$ $-24 \le l \le 24$
Absorption correction	Multiscan	Multiscan
No. of reflections collected	8210	28561
No. of independent reflections	2982	14 149
No. of parameters refined	183	825
Final R_1, wR_2 indices [$I > 2.0\sigma(I)$]	0.0471, 0.1066	0.0513, 0.1159
R_1, wR_2 indices (all data)	0.0858, 0.1305	0.1114, 0.1385
Goodness-of-fit	1.014	1.079
Largest diff. peak and hole (e Å^{-3})	0.382 and −0.421	0.770 and −0.600

*Methanol is from commercial ethanol.

parent atoms. All computations were carried out using SHELXS-97 and SHELXL-97 programs [8]. A PLATON view and ORTEP views were obtained with the WinGx Program System [9]. Details of the data collection and structure refinement parameters are given in table 1. Selected bond distances and angles are listed in table 2 (enaminone **H_2L**) and table 3 (complex **1**).

3. Results and discussion

3.1. *Syntheses of enaminone and its complex*

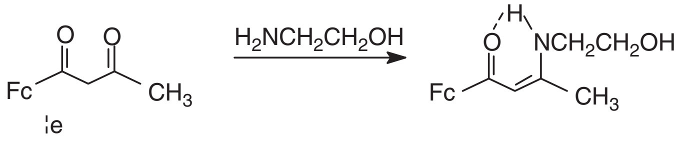
Syntheses of the enaminone and its complex are represented in schemes 1 and 2. Reaction of ferrocenoylacetone [$C_5H_5FeC_5H_4C(O)CH_2C(O)CH_3$] and 2-aminoethanol in refluxing ethanol affords the red enaminone **H_2L** formulated as [$C_5H_5FeC_5H_4C(O)CH{=}C(NHCH_2CH_2OH)CH_3$], not a Schiff base [$C_5H_5FeC_5H_4C(O)CH_2C(NCH_2CH_2OH)CH_3$], in a yield of 94%. The enaminone **H_2L** reacts with copper(II) ion to form the yellow–green complex **1** in a yield of 90%. TLC analyses show that either excess **H_2L** or excess copper(II) ion always leads to the same product.

Table 2. Selected bond distances (Å) and angles (°) for enaminone $\mathbf{H_2L}$.

O(1)–C(11)	1.260(4)	C(11)–C(12)	1.412(5)
O(2)–C(16)	1.408(4)	C(12)–C(13)	1.384(5)
N(1)–C(13)	1.320(4)	C(13)–C(14)	1.501(4)
N(1)–C(15)	1.451(4)	C(15)–C(16)	1.504(5)
C(10)–C(11)	1.480(4)		
O(1)–C(11)–C(10)	118.6(3)	N(1)–C(13)–C(12)	122.1(3)
O(1)–C(11)–C(12)	122.6(3)	N(1)–C(13)–C(14)	117.6(3)
C(10)–C(11)–C(12)	118.8(3)	C(13)–N(1)–C(15)	126.2(3)
C(11)–C(12)–C(13)	120.3(8)	N(1)–C(15)–C(16)	109.7(3)
C(12)–C(13)–C(14)	120.4(3)	O(2)–C(16)–C(15)	109.5(3)

Table 3. Selected bond distances (Å) and angles (°) for complex **1**.

Cu(1)–O(1)	1.914(4)	Cu(3)–O(2)	2.393(4)
Cu(1)–O(2)	1.971(3)	Cu(3)–O(5)	1.920(4)
Cu(1)–O(4)	1.968(4)	Cu(3)–O(6)	1.979(4)
Cu(1)–O(6)	2.463(4)	Cu(3)–O(8)	1.978(4)
Cu(1)–N(1)	1.947(5)	Cu(3)–N(3)	1.940(4)
O(1)–C(11)	1.284(6)	O(5)–C(43)	1.304(6)
C(11)–C(12)	1.399(8)	C(43)–C(44)	1.391(8)
C(12)–C(13)	1.418(7)	C(44)–C(45)	1.415(8)
N(1)–C(13)	1.317(6)	N(3)–C(45)	1.326(7)
N(1)–C(15)	1.490(6)	N(3)–C(47)	1.469(6)
Cu(2)–O(3)	1.919(4)	Cu(4)–O(2)	1.972(4)
Cu(2)–O(4)	1.982(4)	Cu(4)–O(4)	2.472(5)
Cu(2)–O(6)	1.978(4)	Cu(4)–O(7)	1.914(4)
Cu(2)–O(8)	2.447(5)	Cu(4)–O(8)	1.961(4)
Cu(2)–N(2)	1.939(5)	Cu(4)–N(4)	1.941(5)
O(3)–C(27)	1.306(7)	O(7)–C(59)	1.306(6)
C(27)–C(28)	1.386(9)	C(59)–C(60)	1.394(8)
C(28)–C(29)	1.411(9)	C(60)–C(61)	1.426(8)
N(2)–C(29)	1.328(7)	N(4)–C(61)	1.316(6)
N(2)–C(31)	1.472(7)	N(4)–C(63)	1.476(7)
O(1)–Cu(1)–N(1)	95.3(2)	O(6)–Cu(1)–O(4)	74.3(1)
O(2)–Cu(1)–N(1)	84.6(2)	O(1)–C(11)–C(10)	114.4(5)
O(2)–Cu(1)–O(1)	178.1(2)	O(1)–C(11)–C(12)	125.9(5)
O(4)–Cu(1)–O(1)	93.8(2)	C(10)–C(11)–C(12)	119.7(5)
O(4)–Cu(1)–N(1)	168.5(2)	C(13)–N(1)–C(15)	122.1(4)
O(6)–Cu(1)–O(1)	99.4(2)	C(13)–N(1)–Cu(1)	125.2(4)
O(6)–Cu(1)–N(1)	111.1(2)	C(15)–N(1)–Cu(1)	112.3(3)
O(6)–Cu(1)–O(2)	82.4(1)		



Scheme 1. Synthesis of enaminone $\mathbf{H_2L}$.

$$4\mathbf{H_2L} + 4Cu(OAc)_2 \xrightarrow[\text{RT}]{\text{Ethanol}} (\mathbf{L}Cu)_4 + 8\mathbf{H}OAc$$

Scheme 2. Synthesis of complex **1**.

3.2. *Spectra of enaminone and its complex*

Protons of the unsubstituted cyclopentadienyl ring exhibit a singlet at 4.14 ppm in the ^{1}H NMR spectrum of $\mathbf{H_2L}$, whereas protons of the substituted cyclopentadienyl ring appear as two pseudo triplets at 4.34 ppm (3,4-positions) and 4.70 ppm (2,5-positions), respectively. The methine proton displays a singlet at 5.25 ppm. The methyl protons also show a singlet at 1.99 ppm. However, protons of the NCH_2 moiety exhibit a triplet at 3.41–3.46 ppm. Similarly, protons of the OCH_2 moiety display a triplet at 3.79–3.82 ppm with a coupling constant of 5.4 Hz. The NH group appears as a downfield singlet at 10.97 ppm because of intramolecular hydrogen bonding. This evidence is fully consistent with the proposed structure of the ligand shown in scheme 1, and is further supported by its crystal structure [4–7,10–12].

In the IR spectra, complex **1** displays significant changes compared with the ligand. The bands at 3093 and 3270 cm^{-1} in the spectrum of the ligand due to ν(NH) and ν(OH), respectively, do not occur in that of complex **1**. Furthermore, upon coordination, the strong bands assignable to stretching vibrations of the skeleton C=C and C=O groups, which are observed at 1529 and 1595 cm^{-1} in the ligand, respectively, are shifted to 1499 and 1576 cm^{-1} [4–7]. These observations indicate that the enaminone $\mathbf{H_2L}$ is an ONO tridentate ligand, coordinated to the copper ion in the dianionic form (O, carbonyl oxygen, N, deprotonation enamine nitrogen and O, deprotonation alcohol oxygen). Interestingly, the ONO bonding mode is confirmed by the crystal structure of complex **1** (described below).

In the UV spectra of the enaminone $\mathbf{H_2L}$ and complex **1**, three absorptions are observed. The shortest wavelength absorption at 261–273 nm may be assigned to the B-band of the cyclopentadienyl rings and the longest at 445–448 nm to the CT-band. The absorption at 360–366 nm may be attributed to the K-band of the conjugated system. The B- and CT-bands display a hypsochromic shift whereas the K-band shows an inverse shift compared with the free ligand [13]. Like other complexes with ferrocenyl groups, complex **1** has no d–d absorption [13–15].

3.3. *Crystal structure of enaminone H_2L*

Theoretically, enaminones with the general formula [R′(O)CHC(NHR″)R] may have four isomers, E-s-E, E-s-Z, Z-s-E and Z-s-Z, in which E and Z refer to two possible geometric arrangements for the carbon–carbon double bond and s-E and s-Z to isomerism about the carbon–carbon single bond between the carbon–carbon and carbon–oxygen double bonds [7,16,17].

X-ray analysis of the enaminone $\mathbf{H_2L}$ reveals that it is monoclinic, space group $P2_1/c$, and exists in the Z–s–Z form. As shown in figure 1, all atoms in the skeleton O=C–C=C–N are coplanar and can therefore be regarded as sp^2 hybridized. Comparison of the C=O, C–C, C=C and C–N distances (table 2) with the corresponding pure double- or single-bond distances shows that the O=C–C=C–N system is partially delocalized [4,7,17]. The ethylene unit has a gauche conformation, as is usually observed, with a torsion angle of $-52.7(4)^\circ$ for the N(1)–C(15)–C(16)–O(2) group. Intramolecular hydrogen bonding is observed between the carbonyl oxygen and enamine nitrogen [O(1)–N(1) 2.660(4) Å], also in accord with the spectroscopic data [4–7]. Intermolecular hydrogen bonding is found between the hydroxyl hydrogen atom of one molecule and the carbonyl oxygen atom of the other [O(2)–O(1a)

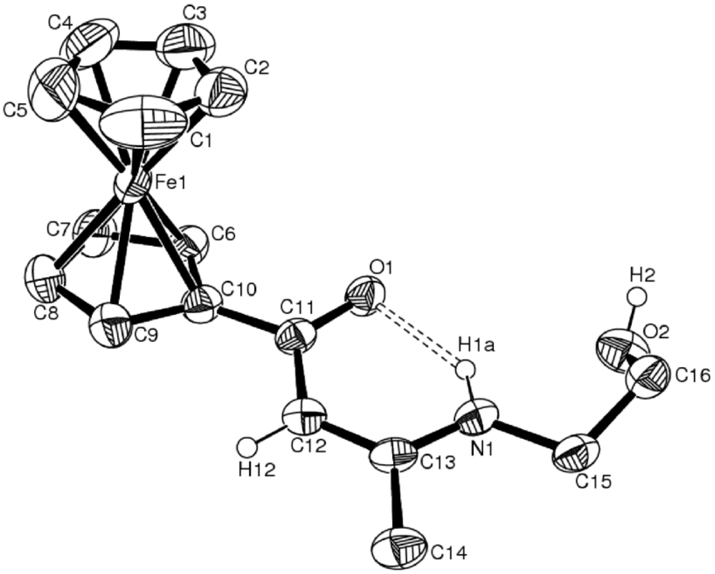


Figure 1. An ORTEP view of enaminone $\mathbf{H_2L}$. Ellipsoids are at 40% probability.

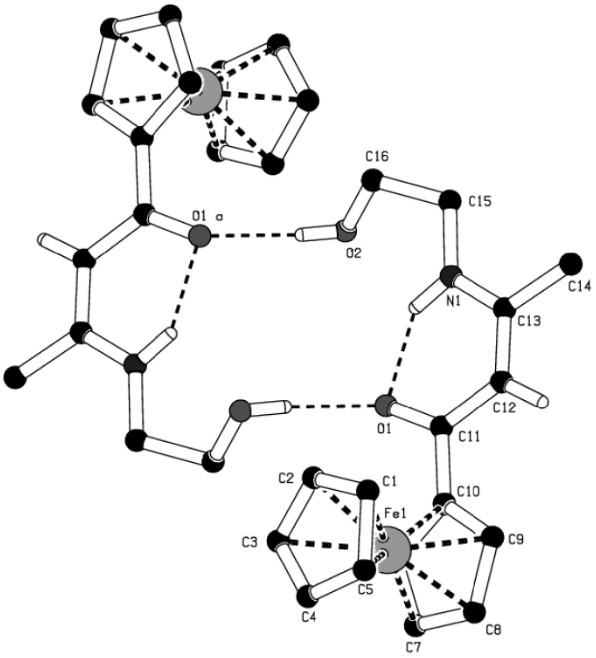


Figure 2. A PLUTON view of a dimer of enaminone $\mathbf{H_2L}$. Symmetry code a: $-x$, $1-y$, $2-z$.

2.694(4) Å; symmetry code a: $-x$, $1-y$, $2-z$] [18]. In the solid state the enaminone $\mathbf{H_2L}$ can dimerize by hydrogen bondings to generate the centrosymmetrical dimer shown in figure 2. The 14-membered ring can be formed in the dimer through both intramolecular and intermolecular hydrogen bonding.

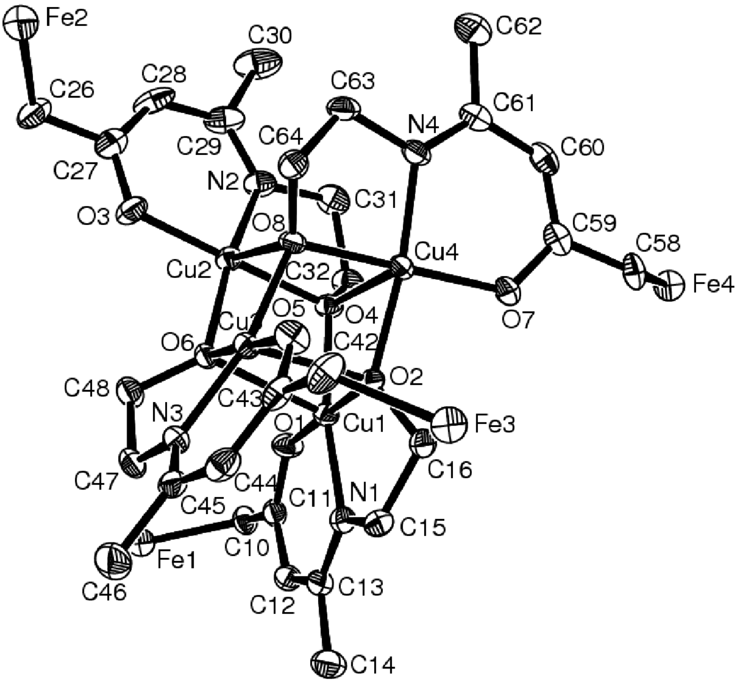


Figure 3. An ORTEP view of complex **1**. Ellipsoids are at 40% probability. The ferrocenyl groups are partly omitted for clarity.

3.4. *Crystal structure of complex 1*

As shown in figure 3, complex **1** contains four subunits (Cu**L**) that are bound together by four bridging alkoxide oxygen atoms to form a cubane-like tetramer with a Cu_4O_4 core. Although Cu_4O_4 complexes of the ideal type may have all the Cu–Cu distances equal and with the highest possible point symmetry S_4, the present complex **1** belongs to the type with the lowest possible point symmetry C_1 [19]. The separations of the copper atoms are all different [Cu(1)···Cu(2) 3.187(4), Cu(1)···Cu(3) 3.272(4), Cu(1)···Cu(4) 3.194(4), Cu(2)···Cu(3) 3.202(4), Cu(2)···Cu(4) 3.339(4) and Cu(3)···Cu(4) 3.143(4) Å]. Furthermore, the geometry within the Cu_2O_2 four-membered rings also shows unsymmetric bridgings; for example, the bond lengths, respectively, are 1.968(4) and 1.982(4) Å for Cu(1)–O(4) and Cu(2)–O(4) and 2.463(4) and 1.978(4) Å for Cu(1)–O(6) and Cu(2)–O(6). For each copper ion, the coordination may be described as a distorted square pyramid with one enamine nitrogen, one carbonyl oxygen and one alkoxide oxygen atom from one ligand ($\mathbf{L}^{2-}$) and two alkoxide oxygen atoms from two neighboring ligands ($\mathbf{L}^{2-}$). The related bond angles are 99.4(2), 97.3(2), 94.0(2) and 101.3(2)° for O(1)–Cu(1)–O(6), O(3)–Cu(2)–O(8), O(5)–Cu(3)–O(2) and O(7)–Cu(4)–O(4), respectively. Table 3 and figure 4 show Cu–O distances in the order $\mathbf{I} < \mathbf{II} < \mathbf{III} < \mathbf{IV}$ for Cu(1), Cu(2) and Cu(3) ions, whereas $\mathbf{I} < \mathbf{III} < \mathbf{II} < \mathbf{IV}$ for the Cu(4) ion. Interestingly, inverse cases appear in a related tetranuclear copper complex [20]. As described above, in each Cu**L** subunit, the enaminone acts as a deprotonated tridentate dianionic ligand ($\mathbf{L}^{2-}$) in which the alkoxide oxygen atom participates in three bridges. The structural features of four $\mathbf{L}^{2-}$ ions (table 3) are

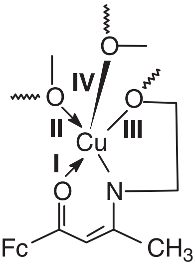


Figure 4. A square pyramidal coordination mode of a Cu(II) ion.

similar; our discussion centers on $\mathbf{L}^{2-}$ from the Cu(1) coordination sphere. The torsion angle of the N(1)–C(15)–C(16)–O(2) group is 44.5(5)°, which is much less than the corresponding value for the free ligand, indicating that the ethylene unit in complex **1** has a more crowded conformation compared with the free ligand. The bond distances of O(1)–C(11), C(11)–C(12), C(12)–C(13) and N(1)–C(13) are 1.284(6), 1.399(8), 1.418(7) and 1.317(6) Å, respectively, whereas the corresponding bond distances of $\mathbf{H_2L}$ are 1.260(4), 1.412(5), 1.384(5) and 1.320(4) Å. These data indicate that, like the ligand, the O=C–C=C–N system of complex **1** is delocalized [4–7]. In the crystalline state, complex **1** is solvated by methanol and dichloromethane; interestingly, molecules of methanol do not participate in the hydrogen bonding because of disorder, whereas the ordered dichloromethane involves formation of a hydrogen bond C(5)–H(5)···Cl(1b) because the C(5)···Cl(1b) distance is 3.77(1) Å (symmetry code b: $1+x$, y, z).

Supplementary data

Crystallographic data have been deposited with the Cambridge Crystallographic Database Centre (CCDC No. 234519 for enaminone $\mathbf{H_2L}$ and CCDC No. 234518 for complex **1**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk; or http://www.ccdc.cam.ac.uk).

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References

[1] J. Kim, J.W. Hwang, Y. Kim, M.H. Lee, Y. Han, Y. Do, *J. Organomet. Chem.* **620**, 1 (2001).

[2] S. Doherty, R.J. Errington, N. Housley, J. Ridland, W. Clegg, M.R.J. Elsegood, *Organometallics* **18**, 1018 (1999).

[3] X.F. Li, K. Dai, W.P. Ye, L. Pan, Y.S. Li, *Organometallics* **23**, 1223 (2004).

[4] Y.C. Shi, H.M. Yang, W.B. Shen, C.G. Yan, X.Y. Hu, *Polyhedron* **23**, 15 (2004).

[5] Y.C. Shi, H.M. Yang, H.B. Song, C.G. Yan, X.Y. Hu, *Polyhedron* **23**, 567 (2004).

[6] Y.C. Shi, W.B. Shen, H.M. Yang, H.B. Song, X.Y. Hu, *Polyhedron* **23**, 749 (2004).

[7] Y.C. Shi, H.M. Yang, H.B. Song, Y.H. Liu, *Polyhedron* **23**, 1541 (2004).

[8] G.M. Sheldrick, *SHELXTL 5.01 Software*, Bruker Analytical X-ray Systems, Madison, WI, USA (1996).
[9] L.J. Farrugia, *WinGx Program System Version 1.64*, University of Glasgow, UK (2003).
[10] J. Mrosset, C. Floriani, M. Mazzanti, A.C. Villa, C. Guastini, *Inorg. Chem.* **29**, 3991 (1990).
[11] M. Kwiatkowski, A. Olechnowicz, J. Mrozinski, D.M. Ho, E. Deutsch, *Inorg. Chim. Acta* **158**, 37 (1989).
[12] H. Iida, Y. Yuasa, C. Kibayashi, Y. Iitaka, *J. Chem. Soc. Dalton Trans.* 2212 (1981).
[13] Y.C. Shi, Q.B. Song, X.L. Wu, Y.X. Ma, *Polyhedron* **13**, 2101 (1994).
[14] Y.C. Shi, Y.M. Liang, X.L. Wu, Q.B. Song, G.S. Huang, Y.X. Ma, *J. Coord. Chem.* **33**, 295 (1994).
[15] Y.C. Shi, *J. Coord. Chem.* **33**, 295 (2004).
[16] L.F. Tietze, A. Bergmann, G. Brill, K. Brugemann, U. Hartfiel, E. Voß, *Chem. Ber.* **122**, 83 (1989).
[17] P. Gilli, V. Bertolasi, V. Ferretti, G. Gilli, *J. Am. Chem. Soc.* **122**, 10405 (2000).
[18] B.E. Douglas, D.H. McDaniel, J.J. Alexander, *Concepts and Models of Inorganic Chemistry*, 2nd Edn, p. 190, John Wiley and Sons, New York (1983).
[19] L. Schwabe, W. Haase. *J. Chem. Soc. Dalton Trans.* 1909 (1985).
[20] H.K. Fun, B.C. Yip, B.L. Song, R.G. Xiong, X.Z. You, *Acta Cryst.* **C51**, 1980 (1995).