

Preparation, Crystal Structure and Properties of a Pentametallic 3-Ferrocenyl-2-crotonic acid-Bridged Copper(II) Complex

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The synthesis and characterization of the copper(II) complex [Cu₅(OOCCH=C(CH₃))Fc(phen)₂](ClO₄)₂·2H₂O (**1**) are reported. The structure of the complex was determined by single-crystal X-ray analysis. The compound crystallizes in the monoclinic system, space group *Pc*, with *Z* = 2, *a* = 1.2799(4) nm, *b* = 0.9969(4) nm, *c* = 2.5228 nm, and β = 91.576(1)°. The cationic part of **1** indicates a pentametallic core in which three 3-ferrocenyl-2-crotonic acid salt (FCA) groups act as (O, O') bridging ligands between two copper(II) ions with a square-pyramidal environment. Cyclic voltammetric experiments in acetonitrile have been performed mainly to examine the Fe(II) → Fe(III) one-electron oxidation in FCA and its complex. The variable-temperature magnetic susceptibility measurements revealed very weak intramolecular anti-ferromagnetic coupling. Fitting parameters are *2J* = -0.2 cm⁻¹, *g* = 2.114, and θ = 0 K.

Keywords crystal structure, Cu(II) complex, magnetic susceptibility

Introduction

Dimeric copper(II) carboxylates containing a variety of oxygen and nitrogen-donor ligands have been extensively investigated and their preparations, magnetic and spectral properties have been reviewed.¹⁻⁵ Different kinds of copper(II) carboxylate adducts have been synthesized and also dinuclear copper(II) complexes have been early studied as useful models to establish magneto-structural correlations for spin exchange between metal ions. In particular, the occurrence of dicopper ions at the active site of the various forms of the oxygen carrier protein hemocyanin in many species of arthropods and mollusks has stimulated much interest in modeling the active-site structure, physicochemical properties, and function of this protein by using model complexes or systems with magnetic coupling inter-

actions.⁶⁻¹⁶ Nevertheless, the number of papers which are focused on polymetallic copper(II) complexes containing ferrocenecarboxylate (-I) anions as ligands is rather scarce.^{6,17-20} Costa *et al.*⁶ showed the structures and properties of [Cu₂(bpy)₂(μ-O₂C)(η⁵-C₅H₄)Fe(η⁵-C₅H₄)₂(ClO₄)(CH₃OH)]⁺ and [Cu₂(bpy)₂(μ-O₂C)(η⁵-C₅H₄)Fe(η⁵-C₅H₄)₂(CH₃OH)]⁺ anions. More recently, [Cu₂(dpt)₂(μ-O₂C)(η⁵-C₅H₄)Fe(η⁵-C₅H₄)₂](ClO₄)₂ containing two dipropylenetriamine and two (O, O') bridging ferrocenecarboxylate ligands have also been synthesized.¹⁷ They are examples of copper(II) complexes containing open-cage-like skeletons [Cu_x(μ-O₂C)_x(L)_y]ⁿ⁺. At present work, we synthesized Fc(C(CH₃)=CHCOOH) as bridging ligands in [Cu_x(μ-O₂CR)_x(L)_y]ⁿ⁺ moieties, in which the ligand has a well electronic delocalization and may bring out nonlinear optical response. In this paper, we report the synthesis, crystal structure, magnetic and electrochemical behavior of the first pentametallic compound in this class containing a [Cu₅(OOCCH=C(CH₃))Fc(phen)₂]⁺ cation.

Experimental

Materials and general methods

3-Ferrocenyl-2-crotonic acid (FCA) was prepared as described previously.²¹⁻²³ Commercially available starting materials of sufficient purity were used without further treatment. Elemental analyses (C, H, N) were carried out at Perkin Elmer 240B. Variable temperature magnetic data (2—300 K) were obtained with a Quantum Design MPMS55 Squid magnetometer operating at 0.1 T. Calibrations were carried out with a palladium standard cylinder,

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and temperature errors were determined with [H₂tmen]⁺[CuCl₄]⁻(H₂tmen = (CH₃)₂HNCH₂CH₂NH(CH₃)₂)⁺.²⁴ The ESR spectrum of **1** was recorded at X-band frequencies (9.46 GHz) with a Bruker ER 2000D-SRC spectrometer in the range 300–4 K. Solid-state diffuse reflectance (190–1000 nm) was recorded on a Shimadzu 310 spectrophotometer. FT-IR spectra (4000–400 cm⁻¹) were recorded on a NEXUS 870 (Nicolet) spectrometer, as KBr pellets. Cyclic voltammograms were obtained on a EG&G PAR 283 potentiostat at 25 °C, using acetonitrile as solvent and 0.1 mol/L Bu₄NClO₄ as supporting electrolyte. The potentials were referred to an Ag-AgCl electrode separated from the solution by a medium-porosity fritted disk. A platinum-wire auxiliary electrode was used in conjunction with a platinum-disk-working electrode. A cyclic voltammogram of a freshly prepared (0.5 mmol/L) solution of **1** in acetonitrile was recorded at 50 mV·s⁻¹ in the -1.0 to 1.2 V range, and the values of **1** and a measured potentials were afterward referred to Ag-AgCl.

Caution! Perchlorate salts of metal complexes are potentially explosive. Only a small amount of material should be handled, and this should be done with caution.

Preparation of {Cu₂(OOCCH=CH(CH₃))₂(phen)₂}ClO₄·2H₂O (**1**)

A solution containing 198 mg (1 mmol) of phen in methanol (15 cm³) was added slowly to the solution formed by Cu(ClO₄)₂·6H₂O (370 mg, 1 mmol) in methanol (5 cm³) with continuous stirring at room temperature. Then, 10 cm³ water was added. After 270 mg (1 mmol) of FCA and 40 mg of sodium hydroxide in 10 cm³ methanol was added. The solution was stirred at room temperature for 2 h and filtered. The product was dissolved in a solvent mixture of dichloromethane and methanol. After slow evaporation of solvent dark brown crystals of **1** appeared. IR ν : 1619, 1579 (COO); 1518, 1450, 1334 (phen); 1103 (ClO₄⁻) cm⁻¹. Anal. calcd for C₆₆H₅₉ClCu₂Fe₃N₄O₁₂: C 55.4, H 4.16, N 3.9; found C 55.3, H 4.1, N 3.9.

X-Ray crystal structure determination of **1**

A dark brown crystal **1** of 0.48 mm × 24 mm × 0.04 mm was selected for X-ray diffraction experiment and mounted on a Siemens SMART 1-K CCD diffractometer. Crystallographic data are summarized in Table 1. The lattice parameters were optimized from least-squares refinement of 25 reflections in the range 2.70° < θ < 28.47° for **1**. Absorption corrections were applied. The minimum and maximum transmission factors were 0.5491 and 0.9454. A total of 22401 reflections were collected (12006 unique, $R_{\text{int}} = 0.11901$). Empirical absorption was applied. The structure was solved by direct methods using SHELXTL program. The positional and the anisotropic thermal parameters of non-hydrogen atoms were refined by full matrix

least squares method of SHELXTL program. The hydrogen atoms were refined isotropically using geometrical constraints with ideal bond lengths and angles and were treated as riding atoms. Their thermal parameters were set at 1.2 times that of their parent atoms. The final R factors were $R_1 = 0.0910$ and $wR = 0.1763$ for $I > 2\sigma(I)$, and the GOF was $F^2 0.939$. A selection of bond lengths and angles is given in Table 2.

Table 1 Crystallographic data of **1**

Empirical formula	C ₆₆ H ₅₉ ClCu ₂ Fe ₃ N ₄ O ₁₂
Formula weight	1430.25
Crystal dimension (mm ³)	0.48 × 0.24 × 0.04
Crystal system	Monoclinic
Space group	Pc
a (nm)	1.280(1)
b (nm)	0.997(1)
c (nm)	2.523(1)
β (°)	91.58(1)
V (nm ³)	3.2179(2)
Z	2
ρ_{calcd} (g·cm ⁻³)	1.476
λ (nm)	0.071073
Temperature (K)	293(2)
$R_1 [I > 2\sigma(I)]^a$	0.0910
$wR_2 [I > 2\sigma(I)]^a$	0.1763

$$^a R_1 = \frac{\sum \|F_0| - |F_C|\|}{\sum |F_0|}, wR_2 = \left[\frac{\sum w(|F_0|^2 - |F_C|^2)^2}{\sum w|F_0|^2} \right]^{1/2}.$$

Table 2 Selected bond distances (nm) and angles (°) for **1**

Cu(1)—O(6)	0.1933(6)
Cu(1)—O(3)	0.1976(5)
Cu(1)—N(2)	0.1995(7)
Cu(1)—N(1)	0.2014(6)
Cu(1)—O(1)	0.2390(5)
Cu(2)—O(1)	0.1907(6)
Cu(2)—O(5)	0.1946(6)
Cu(2)—N(3)	0.1997(7)
Cu(2)—N(4)	0.2052(7)
Cu(2)—O(3)	0.2335(5)
O(1)—O(57)	0.1316(9)
O(2)—O(57)	0.1171(9)
O(4)—O(60)	0.1270(9)
O(5)—O(60)	0.1238(10)
O(7)—O(63)	0.1280(11)
O(6)—Cu(1)—O(3)	92.8(2)
O(6)—Cu(1)—N(2)	168.2(3)
O(3)—Cu(1)—N(2)	97.2(2)
O(6)—Cu(1)—N(1)	89.3(3)
O(3)—Cu(1)—N(1)	171.1(2)
N(2)—Cu(1)—N(1)	81.9(3)
O(6)—Cu(1)—O(1)	89.5(2)
O(3)—Cu(1)—O(1)	79.25(19)
N(2)—Cu(1)—O(1)	86.0(2)

Continued

N(1)-Cu(1)-O(1)	109.5(2)
O(1)-Cu(2)-O(5)	94.5(2)
O(1)-Cu(2)-N(3)	172.9(3)
O(5)-Cu(2)-N(3)	90.2(3)
O(1)-Cu(2)-N(4)	91.9(3)
O(5)-Cu(2)-N(4)	172.8(3)
N(3)-Cu(2)-N(4)	83.1(3)
O(1)-Cu(2)-O(3)	82.0(2)
O(5)-Cu(2)-O(3)	91.8(2)
N(3)-Cu(2)-O(3)	103.1(2)
N(4)-Cu(2)-O(3)	92.4(2)
Cu(1)-O(3)-Cu(2)	94.0(19)
Cu(2)-O(1)-Cu(1)	94.1(2)
O(2)-O(5)-O(1)	125.7(7)
O(6)-O(3)-O(5)	127.5(9)
O(4)-O(6)-O(3)	119.4(8)

Results and discussion

Description of the crystal structures

The crystal structure of $\{\text{Cu}_2(\text{OOCCH}=\text{C}(\text{CH}_3)\text{Fc})_2(\text{phen})_2\}[\text{ClO}_4 \cdot 2\text{H}_2\text{O}]$ (**1**) is depicted in Fig. 1, and the relevant bond distances and angles are listed in Table 2. The cation consists of two phen ligands, three FCAs and two copper atoms, which have a five-coordinate environment. Oxygen atoms from FCA groups and two nitrogen atoms from the chelating phen ligands define the basal plane. The coordination geometry is confirmed by evaluation of Addison's parameter.²⁵ The ratio of the basal angles, τ , defined as $\tau = [(\theta - \phi)/60] \times 100$, represents the percentage trigonal distortion from square pyramidal geometry. For an ideal square pyramid, τ is 0. While for an ideal trigonal bipyramid τ is 100. The relevant angles in molecule **1**, $\theta = 171.1(2)^\circ$ and $172.9(3)^\circ$ and $\phi = 168.2(3)^\circ$ and 172.8° , yield τ values of 4.8% and 0.16%, which show that the two copper atoms have square pyramidal environment with a slight trigonal-bipyramidal distortion.

Three carboxylate bridges link the copper atoms. One of the cation carboxylate groups takes the familiar bidentate $\eta:\eta:\mu$ bridging mode, and the others are in the rare monoatomic bridging mode; two nitrogen atoms of the terminal phen molecule complete the five-coordination at each copper(II) atom. The unusual bridging mode for the carboxylates results in a difference between the length of the carboxylate CO bonds, namely: the C(57)-O(1) distance [0.1316(9) nm] longer than the O(57)-O(2) [0.1171(9) nm] and the O(60)-O(4) distance [0.1270(9) nm] longer than the O(60)-O(5) [0.1238(10) nm]. The Cu...Cu intradimer distance is 0.316 nm, similar to those reported in the two dinuclear cations of complex $[\text{Cu}_2(\text{bpy})_2(\mu\text{-O}_2\text{C}(\eta^5\text{-C}_5\text{H}_4)\text{Fc}(\eta^5\text{-C}_5\text{H}_4))_2(\text{ClO}_4)(\text{CH}_3\text{OH})]$ **I** $[\text{Cu}_2(\text{bpy})_2(\mu\text{-O}_2\text{C}(\eta^5\text{-C}_5\text{H}_4)\text{Fc}(\eta^5\text{-C}_5\text{H}_4))_2(\text{ClO}_4)(\text{CH}_3\text{OH})]$.

$\text{C}_5\text{H}_4\text{Fc}(\eta^5\text{-C}_5\text{H}_4)_2(\text{CH}_3\text{OH})_2](\text{ClO}_4)_3$.⁶ In this cation, the fragment Cu-O-C-O-Cu is nearly planar, and the bite angle of the carboxylate is 127.5° , while the Cu-O-Cu angles range from 94.02° to 94.1° . Obviously, the Cu-O-Cu angles are smaller than that of $[\text{Cu}_2(\text{O}_2\text{CCH}_3)_2(\text{bpy})_2](\text{ClO}_4)_2$.²⁶ The average Fe-C_{ring} and C-C_{ring} bond lengths of ferrocenyl units are similar to those reported in the literature.^{27,28} The Fe-C_{ring} distances range from 0.1925(4) nm to 0.2151(4) nm (average 0.2031 nm).

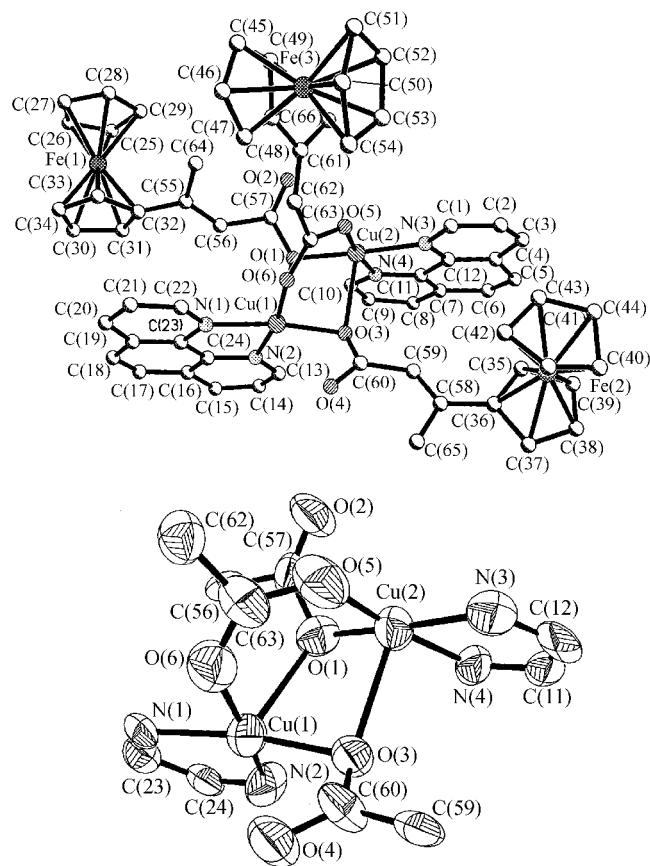


Fig. 1 Molecular structure of the title complex (top) and scheme around the Cu atoms (bottom). Hydrogen atoms, anion and solvent molecule have been omitted for clarity.

An examination of the bond bridging connections between the copper ions shows that O(1) and O(3) form short equatorial contacts within the copper square-pyramids [Cu(1)-O(3) 0.1976 nm; Cu(2)-O(1) 0.1907 nm], and long axial contacts [Cu(1)-O(1) 0.2390 nm; Cu(2)-O(3) 0.2335 nm], leading to magnetic orbital orthogonality between the metal centers. The bidentate bridging carboxylate links the copper ions via short equatorial contacts [Cu(1)-O(6) 0.1933 nm; Cu(2)-O(5) 0.1946 nm], leading to a situation where antiferromagnetic exchange can take place (vide infra).

Spectroscopy

Solid state Nujol mull transmittance electronic spectra

for **1** give a broad visible band at about 620 nm and a lower energy shoulder, consistent with the effectively five-coordinate geometry observed at the copper(II) centers. The spectrum agrees with those previously reported for $[\text{Cu}(\text{NH}_3)_5]^{2+}$.²⁹ This result may demonstrate that complex **1** has a square pyramidal geometry, instead of the trigonal bipyramid. The assignment of the electronic reflectance spectra of copper(II) has been extensively discussed in the literature.²⁹⁻³⁴ It would be reasonable to assign the intense band of complex **1** at 620 nm as the d_{xz} , $d_{yz} \rightarrow d_{x^2-y^2}$ transition and the shoulder as the $d_z^2 \rightarrow d_{x^2-y^2}$ transition. This assignment is in agreement with that suggested for other square-based pyramidal copper(II) complexes.^{32,34}

Magnetic susceptibility and ESR studies

Variable temperature magnetic susceptibility measurement was carried out on a powdered sample of the complex taken from the uniform batch used for structural determination in the temperature range of 2–300 K. The room temperature magnetic moment for **1** ($1.87 \mu_B$) is close to the normal value for an uncoupled copper(II) system, and might suggest the absence of spin exchange. However the magnetic moment is greater than $1.83 \mu_B$ above 16 K, and drops to $1.75 \mu_B$ at 2 K, indicating the possible presence of very weak antiferromagnetic coupling (Fig. 2). The variable temperature magnetic susceptibility data were fitted to the Bleaney-Bowers equation³⁵ (Eq. (1)); J is the exchange integral, ρ is the fraction of paramagnetic impurity, θ is a Weiss-like corrective term, N_a is the temperature independent paramagnetism, and the other terms have their usual meaning; the equation is based on the Hamiltonian $H = -2JS_1S_2$ to give $g = 2.114(7)$, $2J = -0.23(3) \text{ cm}^{-1}$, $\rho = 0.0045$, $N_a = 60 \times 10^{-8} \text{ cm}^3 \cdot \text{mol}^{-1}(\text{Cu})$, $\theta = 0 \text{ K}$, $10^2 R = 0.25 (R = [\sum \chi_{\text{obs}} - \chi_{\text{calc}}]^2 / \sum \chi_{\text{obs}}^2)^{1/2}$.

$$\chi_M = \frac{Ng^2\beta^2}{\kappa(T - \theta)} \left[\frac{1}{3 + \exp(-2J/\kappa T)} \right] (1 - \rho) + \left[\frac{Ng^2\beta^2}{4\kappa T} \right] \rho + N_a \quad (1)$$

The three bridges present in **1** should be considered in context regarding the magnetic properties. The orthogonal bridging connections via the μ -O carboxylates will not contribute any anti-ferromagnetic exchange, but may lead to a ferromagnetic exchange component.³⁶ The equatorial *syn-syn* carboxylate bridge is positioned appropriately for anti-ferromagnetic exchange coupling, and so the net weak antiferromagnetic exchange in **1** can reasonably be considered as the sum of two opposing exchange terms, with the antiferromagnetic term being slightly larger.

Fig. 3 represents the ESR spectra of **1** in DMF solution at 300 K and 100 K. Frozen solution ESR spectra well resolved axial $S = 1/2$ spectra with superhyperfine splitting superimposed on the equatorial absorptions. It can be seen

that the spectrum of the complex is split into four equally spaced absorptions by the interaction of the unpaired electron with the Cu(II) nucleus at 300 K. The isotropic ESR parameters are $g_{\text{iso}} = 2.066$ and $A_{\text{iso}} = 88.3 \text{ G}$. The approximate ESR parameters of complex **1** are graphically evaluated as $g_{\parallel} = 2.2071$, $g_{\perp} = 1.9959$, $A_{\parallel} = 191.0 \text{ G}$ and $A_{\perp} = 36.9 \text{ G}$, where $g_{\perp} = (3g_{\text{iso}} - g_{\parallel})/2$ and $A_{\perp} = (3A_{\text{iso}} - A_{\parallel})/2$. The value of g_{iso} is close to the value obtained from the susceptibility data.

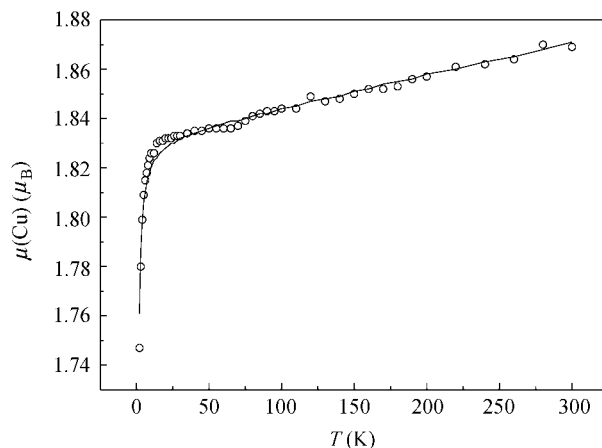


Fig. 2 Variable temperature magnetic data for complex **1**. The solid line was calculated from Eq. (1).

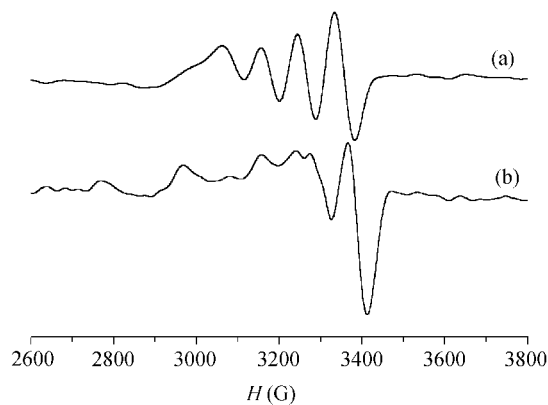


Fig. 3 X-Band ESR spectra of **1** in DMF at (a) 300 K and (b) 100 K.

Electrochemical studies

The cyclic voltammogram of **1** in the anodic zone displays one signal with a directly associated peak in the reverse scan ($E_{1/2} = 0.53 \text{ V}$, $\Delta E = 75 \text{ mV}$) which is assigned to the envelope of the $\text{Fe}(\text{II}) \rightarrow \text{Fe}(\text{III})$ redox processes of the coordinated ferrocenecarboxylate groups. When the cyclic voltammogram was recorded in the cathodic area, one irreversible reduction peak was detected at -0.67 V . This redox behavior exhibits a unique quasi-reversible cathodic process due to the $\text{Cu}(\text{II}) \rightarrow \text{Cu}(\text{I})$ couple (Fig. 4).

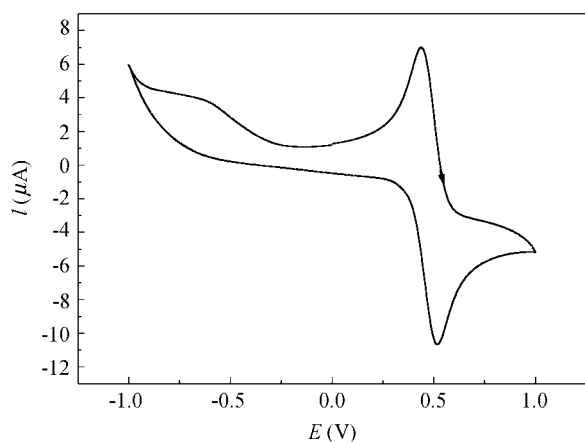


Fig. 4 Cyclic voltammogram of **1** in $\text{CH}_3\text{CN}/\text{Bu}_4\text{NClO}_4/\text{Pt}$ vs. SCE at 20° , scan rate = $52 \text{ mV} \cdot \text{s}^{-1}$.

Conclusions

The coordination chemistry of copper(II) has been extensively studied and well understood. Especially for binuclear complexes with carboxylate ligands, the coordination modes show a rich variety of structure motifs, giving the opportunity for a better understanding of Cu(II) behavior. In this paper, a novel motif of a binuclear three-carboxylato copper(II) complex with three bridging and two phen ligands is reported. This structure shows a Cu(II)...Cu(II) distance of 0.316 nm, and the complex exhibits very weak intramolecular antiferromagnetic exchange.

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