# Synthesis, Characterization and Crystal Structure of the First Trinuclear MFe₂ (M = Cu and Ni) Complexes Based on Nitroprusside

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Three new complexes, Ni(H₂L)[Fe(CN)₅NO]₂·6H₂O (**1**), Ni(H₂L)[Fe(CN)₅NO]₂·4H₂O (**2**) and Cu(H₂L)[Fe(CN)₅NO]₂·4H₂O (**3**) (L = 3,10-bis(2-aminoethyl)-1,3,5,8,10,12-hexaazacyclotetradecane) are prepared and characterized by IR, elemental analyses and single-crystal X-ray analyses, indicating that they are the first examples of trinuclear nitroprusside-bridged MFe₂ (M = Cu and Ni) complexes. In the three complexes, the central metal atoms (M) are all six-coordinated by the nitrogen atoms from the macrocyclic ligand and two cyano-bridges at the trans-positions to form distorted octahedral configurations. The axial N—M—N linkage is nearly vertical to the equatorial plane defined by four coordinating N atoms of macrocyclic ligand. The C≡N—Ni bond angle of 172.6° in compleox **1** is apparently larger than those in complexes **2** and **3** (152.57° and 136.37°, respectively). The three complexes are all connected by hydrogen bonds into 3D networks. This study shows that the cyano-bridged trinuclear species could be generated via the control of the charge of the building blocks.

**Keywords**    copper complex, nickel complex, nitroprusside, cyano bridge, crystal structure

## Introduction

Since 1848, when Playfair published the first paper related to nitroprussides,[1] the transition metal pentacyanonitrosylmetallate hydrates have been widely studied because of their important roles in molecular sieves, cation exchangers, electron scavengers and radionuclide sorbents.[2-4] The nitroprussides, regardless of the cationic metal, are currently employed as reversible inhibitors of a group of enzymes known as superoxide dismutases.[5]

Recently, using $[Fe(CN)_5NO]^{2-}$ as a building block, some nitroprusside-bridged polymeric complexes have been prepared and magnetic studies showed that the nitroprusside anion transmits a very weak antiferromagnetic interaction.[6-8] Currently, there has been a growing interest in clarifying the structural correlation with magnetic properties of nitroprusside-bridged complexes. Tang and co-

workers reported an antiferromagnetic 2-D cyano-bridged polymeric {Cu₂(oxpn)[Fe(CN)₅NO]}ₙ (H₂oxpn = $N$, $N'$-bis(3-aminopropyl)oxamide) complex, in which a nitrogen atom of the cyano group in $[Fe(CN)_5NO]^{2-}$ was coordinated to one of the adjacent copper(II) ions in [Cu₂-oxpn]²⁺.[9] The complexes {M(en)₂Fe(CN)₅NO·$n$H₂O} where en = ethylenediamine, M = Ni(II)[6] and Cu(II),[7] $n$ = 0 or 1) are one-dimensional and {Cu(L)₂Fe(CN)₅NO·$n$H₂O} (where L = 2-dimethylaminoethylamine,[10] 1-dimethylamino-2-propylamine,[10] 3,10-bis(2-hydroxyethyl)-1,3,5,8,10,12-hexaazacyclotetradecane[8] and 1,2-diaminopropane[11]) are cyano-bridged binuclear complexes.

In order to synthesize nitroprusside-bridged complexes with new structures,[12] we modified the four-coordinate ML$^{n+}$ (M = Cu and Ni) cation from common divalent to tetravalent[13] and successfully obtained the first three trinuclear nitroprusside-bridged complexes with the formula of MFe₂ (M = Cu and Ni). The complexes Ni(H₂L)[Fe(CN)₅NO]₂·6H₂O (**1**), Ni(H₂L)[Fe(CN)₅NO]₂·4H₂O (**2**) and Cu(H₂L)[Fe(CN)₅NO]₂·4H₂O (**3**) (L = 3,10-bis(2-aminoethyl)-1,3,5,8,10,12-hexaazacyclotetradecane) are all characterized by IR, elemental analyses and single-crystal X-ray analyses.

## Results and discussion

Employing Ni(H₂L)(ClO₄)₄, Ni(H₂L)Br₄ and Cu(H₂L)(ClO₄)₄ as reagents to react with Na₂[Fe(CN)₅NO]·2H₂O leads to three trinuclear complexes **1**, **2** and **3**, respectively. The assembly of the trinuclear molecules is probably due to the charge ratio of two building blocks. Of course, a structure consisting of one-dimensional nitroprusside-bridged alternating Ni-Fe chain with a free nitroprusside anion may be generated as a variation of the trinuclear cluster. Such a case has been seldom observed.

*Crystal structures*

nitroprussides.[7-9]

The selected bond lengths and angles are listed in Table 1.

As shown in Fig. 1 the structure of complex **1** consists of a trinuclear cyano-bridged $NiFe_2$ molecules and lattice water molecules in which the central Ni atom is coordinated by six N atoms to form a slightly distorted octahedron configuration. Four of the six N atoms which defined the equatorial plane are from $H_2L^{2+}$ ligand with the average $Ni-N_{equatorial}$ distance of 0.2066 nm and the N 7 — Ni 1 —N 8 angle of 85.4°. The other two N atoms at the axis are from the two cyano-bridges of two Fe CN ₅- NO ²⁻ ions with the $Ni-N_{axial}$ distance of 0.2113 6 nm. While in the one-dimensional complex Ni en ₂Fe- CN ₅ NO ⁶ the Ni—N bond lengths ranging from 0.2095 to 0.2099 nm are almost the same. In complex **1** the axial N—Ni—N linkage are linear and almost vertical to the equatorial plane which can be approved by the angles of N 7 -Ni 1 -N 1 88.5 2 ° N 8 -Ni 1 - N 1 90.9 2 °. The C 1 -N 1 -Ni 1 angle of 172.6 6 ° is nearly linear and apparently lager than that of complex Ni en ₂ Fe CN ₅ NO ₆ and most of the Cu - Fe
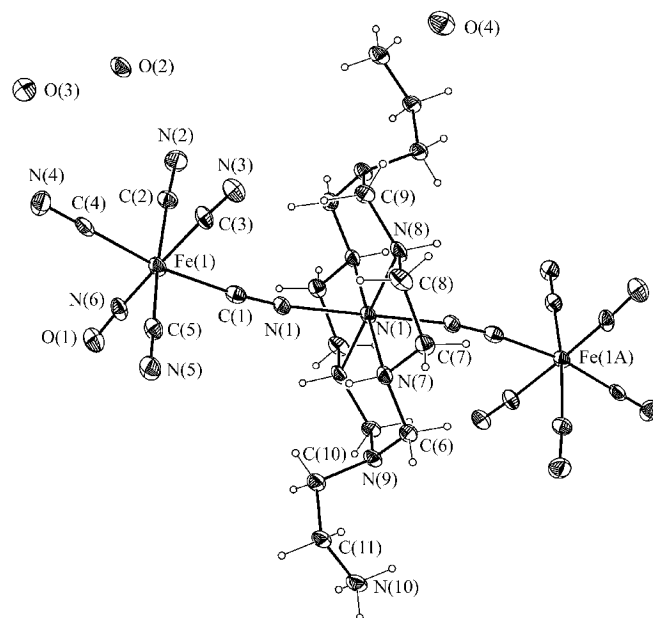


**Fig. 1** ORTEP drawing of **1** with atomic numbering scheme showing thermal ellipsoids at the 30% probability level.

**Table 1** Selected bond lengths nm and angles ° of **1** **2** and **3**

|  | **1** | **2** | **3** |  |
|---|---|---|---|---|
| Ni 1 —N 1 | 0.2113 6 | 0.2135 2 | Cu 1 —N 1 | 0.2506 3 |
| Ni 1 —N 7 | 0.2062 5 | 0.20567 19 | Cu 1 —N 7 | 0.2008 3 |
| Ni 1 —N 8 | 0.2070 6 | 0.2059 2 | Cu 1 —N 8 | 0.2016 2 |
| Fe 1 —C 1 | 0.1940 7 | 0.1932 2 | Fe 1 —C 1 | 0.1942 3 |
| Fe 1 —C 2 | 0.1946 7 | 0.1938 3 | Fe 1 —C 2 | 0.1945 4 |
| Fe 1 —C 3 | 0.1947 8 | 0.1941 3 | Fe 1 —C 3 | 0.1950 4 |
| Fe 1 —C 4 | 0.1941 8 | 0.1934 3 | Fe 1 —C 4 | 0.1941 4 |
| Fe 1 —C 5 | 0.1929 7 | 0.1941 3 | Fe 1 —C 5 | 0.1941 4 |
| Fe 1 —N 6 | 0.1649 7 | 0.1662 2 | Fe 1 —N 6 | 0.1660 3 |
| O 1 —N 6 | 0.1139 8 | 0.1126 3 | O 1 —N 6 | 0.1133 4 |
| N 1 —C 1 | 0.1131 8 | 0.1143 3 | N 1 —C 1 | 0.1141 4 |
| C 1 -N 1 -Ni 1 | 172.6 6 | 152.57 19 | C 1 -N 1 -Cu 1 | 136.37 |
| N 7 -Ni 1 -N 8 | 85.4 2 | 85.52 8 | N 7 -Cu 1 -N 8 | 86.10 10 |
| N 7 -Ni 1 -N 1 | 88.5 2 | 92.85 8 | N 7 -Cu 1 -N 1 | 88.10 10 |
| N 8 -Ni 1 -N 1 | 90.9 2 | 89.04 8 | N 8 -Cu 1 -N 1 | 91.82 10 |
| N 6 -Fe 1 -C 1 | 96.2 3 | 95.49 10 | N 1 -C 1 -Fe 1 | 179.5 3 |
| N 6 -Fe 1 -C 2 | 97.7 3 | 96.90 12 | N 2 -C 2 -Fe 1 | 176.7 4 |
| N 6 -Fe 1 -C 3 | 176.8 3 | 177.53 12 | N 3 -C 3 -Fe 1 | 176.6 3 |
| N 6 -Fe 1 -C 4 | 94.8 3 | 93.26 11 | N 4 -C 4 -Fe 1 | 175.9 3 |
| N 6 -Fe 1 -C 5 | 91.5 3 | 96.19 11 | N 5 -C 5 -Fe 1 | 176.9 3 |
| O 1 -N 6 -Fe 1 | 175.5 6 | 179.0 2 | O 1 -N 6 -Fe 1 | 179.4 3 |
| N 1 -C 1 -Fe 1 | 174.4 7 | 174.9 2 | N 6 -Fe 1 -C 1 | 93.28 13 |
| N 2 -C 2 -Fe 1 | 176.5 7 | 177.3 3 | N 6 -Fe 1 -C 2 | 96.81 15 |
| N 3 -C 3 -Fe 1 | 176.4 7 | 175.6 3 | N 6 -Fe 1 -C 3 | 178.20 15 |
| N 4 -C 4 -Fe 1 | 177.9 7 | 176.0 3 | N 6 -Fe 1 -C 4 | 93.48 14 |
| N 5 -C 5 -Fe 1 | 179.1 7 | 177.2 2 | N 6 -Fe 1 -C 5 | 96.82 14 |

As usual the Fe CN $_5$ NO $^{2-}$ moiety exhibits a distorted octahedral structure with the mean Fe—C Fe—N N—O and C—N bond lengths of 0.1941 0.1649 0.1145 and 0.1139 nm respectively. The Fe-C-N and Fe-N-O bond angles range from 174.4° to 179.1°. These values are in good agreement with those in the previous reports.[6 10]

As shown in the unit cell plot Fig. 2 of complex **1** all the NiFe$_2$ units align in the same direction and are parallel to each other to form a well-arranged ordered structure.

The molecules are connected by N—H…N and N—H …O hydrogen bonds leading to a 3D network. The N 10 atom of the NH$_3^+$ group and the N 8 atom coordinated with the Ni center are involved in the N—H…O$_{water}$ hydrogen bonds with the N…O distances ranging from 0.2825 to 0.3136 nm. The N 5 atom of the Fe CN $_5$ NO $^{2-}$ anion and the N 7 atom in the macrocyclic ligand are connected by the hydrogen bond with N…N distance of 0.3029 nm and N—H…N angle of 146.67°.



**Fig. 3** ORTEP drawing of **2** with atomic numbering scheme showing thermal ellipsoids at the 30% probability level.



**Fig. 2** Unit cell packing diagram of **1**. Hydrogen bonds are indicated by broken lines.
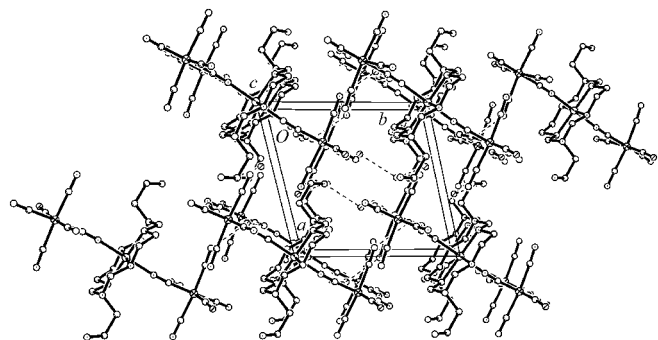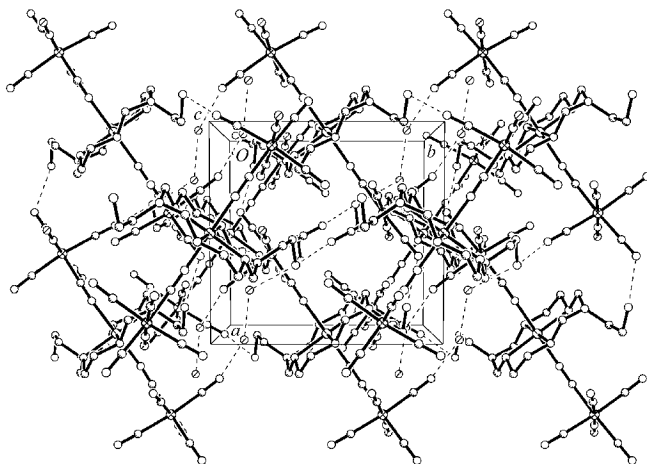


**Fig. 4** Unit cell packing diagram of **2**. Hydrogen bonds are indicated by broken lines.

Fig. 3 shows the ORTEP plot of complex **2**. The crystal structure of complex **2** is similar to that of complex **1** with the difference in the number of free H$_2$O molecules and the bond distances and angles. The C 1 -N 1 -Ni 1 bond angle of 152.57 19 ° is obviously smaller than that of complex **1** but in accordance with that in other analogs.

Complexes **1** and **2** belong to the different space groups $P\overline{1}$ and $P2_1/n$ respectively which indicates that they have different packing modes Fig. 4 . The spatial configuration of complex **2** can be described as interlaced 2D layers. All the NiFe$_2$ units of the same layer are parallel but not parallel to those of the adjacent two layers.

Complex **2** also forms a 3D network via hydrogen bonds but the situations are different form that of complex **1**. The N 10 atom of NH$_3^+$ anion is not only connected with O 2 $_{water}$ atom but also connected with N 4 and N 5 atoms of Fe CN $_5$ NO $^{2-}$ anion by hydrogen bonds. The N 7 and N 8 atoms of macrocyclic ligand are connected with N 3 atom of the nearby trinuclear molecule and the O 3 $_{water}$ atom respectively via hydrogen bonds.
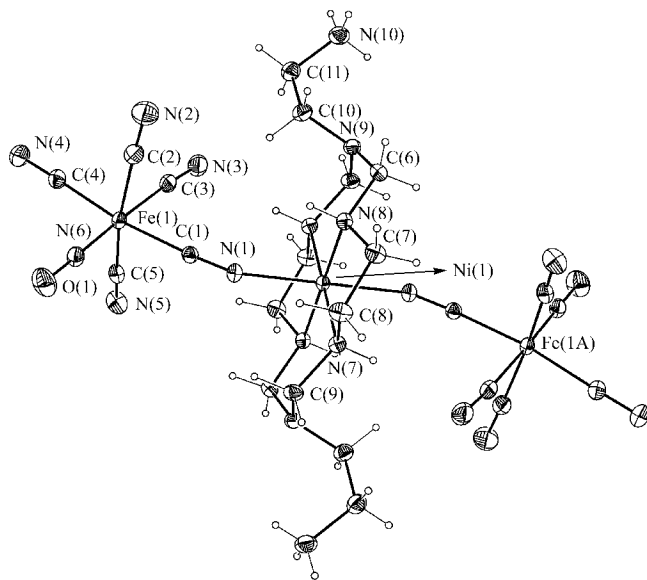
The ORTEP drawing of complex **3** is illustrated in Fig. 5. Complex **3** is isomorphous with complex **2**. The central Cu atom is also six-coordinated by N atoms leading to a distorted octahedron structure with four N atoms from the L ligand defining the equatorial plane and two N atoms from two bridging CN$^-$ ligands occupying the axial positions. The Cu—N$_{equatorial}$ bond lengths ranging from 0.2008 to 0.2016 nm is shorter than the Cu—N$_{axial}$ bond lengths 0.2506 nm due to the Jahn-Teller effect for the d$^9$ configuration of the Cu II ion in an octahedral environment. The bridging cyanides are coordinated to the Cu II ions in a bent fashion with the C 1 -N 1 -Cu 1 bond angle of 136.37° which is similar to that of Cu en $_2$Fe CN $_5$ NO .[7] The mean bond lengths and angles of Fe CN $_5$ NO $^{2-}$ anion are in accordance with the corresponding values in complexes **1** and **2** Table 1 .

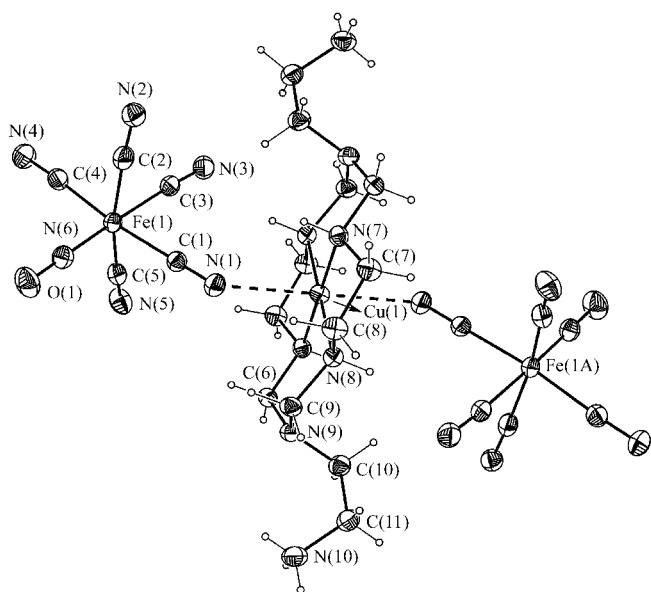**Fig. 5** ORTEP drawing of **3** with atomic numbering scheme ( show-ing thermal ellipsoids at the 30% probability level ).

The packing mode and the hydrogen bonds of complex **3** is almost the same as that of complex **2** ( except some slight difference in bond lengths and angles ).

*Spectroscopic properties*

Generally , IR absorption bands in the region 2200— 1900 $cm^{-1}$ are due to the C≡N and N = O stretching vi-brations . Complexes **1** , **2** and **3** show strong band at 1937 , 1947 and 1924 $cm^{-1}$ respectively , which is reasonably assigned to the $NO^+$ stretching vibration . Strong bands at 2145 , 2146 and 2144 $cm^{-1}$ which indicates the stretching vibration of terminal $CN^-$ are observed for complexes **1** , **2** and **3** , respectively . Since the formation of the cyano bridge shifts $\nu$ ( CN ) towards higher frequency , the peaks at 2176 and 2169 $cm^{-1}$ for complexes **1** and **2** respective-ly strongly demonstrate the presence of cyano bridges . There is no obvious peak observed at *ca* . 2170 $cm^{-1}$ in complex **3** , which may be due to the weakness of interac-tion between $CN^-$ and Cu ( II ) .

UV-vis spectra of **1** and **2** in aqueous solution are identical and exhibit a strong absorption with the $\lambda_{max}$ at 200 nm ( $\varepsilon$ = 1500 $mol^{-1}$ L $cm^{-1}$ ) and a shoulder at 255 nm ( $\varepsilon$ = 20 $mol^{-1}$ L $cm^{-1}$ ) which are assigned to the ligand-to-metal charge transfer transition of [ Fe ( CN )$_5$- NO ]$^{2-}$ . Very weak signals near 400 nm can be due to the d-d transitions of the Ni ( II ) ions . UV-vis spectrum of **3** in aqueous solution exhibits a weak asymmetrical broad absorption with the $\lambda_{max}$ at 514 nm ( $\varepsilon$ = 1.5 $mol^{-1}$ L $cm^{-1}$ ) which is assigned to d-d transition of the Cu ( II ) ions . Compared with the UV-vis spectrum of the Cu ( II ) precursor [14] substitution of isocyano- for perchlorato-ligand shifts the band by 12 nm towards higher frequencies , as would be expected from spectrochemical considerations .

Considering that the nitroprusside group is diamagnet-

ic , the electron paramagnetic resonance ( EPR ) spectra of **3** may provide some useful information about the electronic structure of the Cu ( II ) ion . The powder X-band EPR spectrum measured at room temperature showing hyperfine splitting around the $g_{//}$ region is typical of an isolated $d^9$ complex ( Fig. 6 ) . Analysis of the spectrum affords param-eters of $g_{//}$ = 2.19 and $A_{//}$ = 200 G which are in good a-greement with those for mononuclear copper ( II ) com-pounds.[14,15] The spectrum is very similar to that for the precursor [ Cu ( $H_2L$ ) ] ( $ClO_4$ )$_4$.[14] This is understandable considering that both complexes possess similar Cu ( II ) co-ordination surroundings ( $CuN_6$ for **3** and $CuN_4O_2$ for [ Cu-( $H_2L$ ) ] ( $ClO_4$ )$_4$ ) . The EPR spectrum in an aqueous solu-tion exhibits four isotropic hyperfine peaks with the param-eters of $a_{iso}$ = 90 G and $g_{iso}$ = 2.10 .



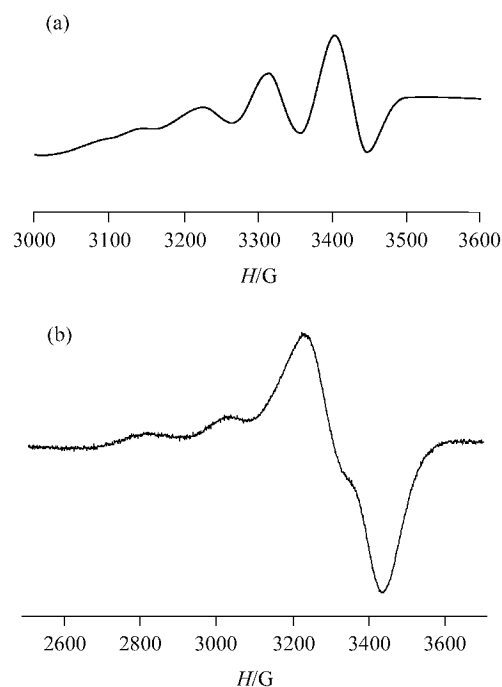**Fig. 6** EPR spectra of **3** recorded at room temperature ( a aque-ous solution ; b solid ) .

In conclusion , the results showed that new cyano-bridged trinuclear species could be generated via the con-trol of the charge of the building blocks . It can be there-fore anticipated that other trinuclear $NiM_2$ containing para-magnetic [ Cr ( CN )$_6$ ]$^{3-}$ or [ Fe ( CN )$_6$ ]$^{3-}$ and hexavalent $Ni^{II}H_4L$[6+] precursors could be prepared . Further work along this line is in progress in our laboratory .

## Experimental

Elemental analyses of carbon , hydrogen and nitrogen were carried out with an Elementar Vario EL . The infrared spectroscopy was performed on a Magna-IR 750 spec-trophotometer in the 4000—400 $cm^{-1}$ region . The elec-tronic spectra of **1**—**3** were measured with a Perkin Elmer Hitachi-240 spectrophotometer in water . The room-temper-

ature EPR spectra of **3** were recorded at X-band with a Bruker ER 200B spectrometer.

Cu  H₂L    ClO₄  ₄ and Ni  H₂L    ClO₄  ₄ were prepared by the reported method.[14 16] Ni  H₂L    Br₄ is prepared by a method similar to  Ni  H₂L    ClO₄  ₄ except employing HBr to take the place of HClO₄.

*Complex* **1**    Slow evaporation of the aqueous solution of  Ni  H₂L    ClO₄  ₄ and Na₂ Fe CN  ₅ NO  · 2H₂O  molar ratio  1∶1  at room temperature resulted in the light brown crystals suitable for single crystal analysis. UV-vis  H₂O  $\lambda_{max}$  200  255  400 nm  IR  ν  2169 2146  1947 cm⁻¹. Anal. calcd for NiFe₂C₂₂N₂₀H₄₆O₈  C 29.72  H 5.21  N 31.51  found C 29.57  H 5.10  N 31.46.

*Complex* **2**      Light brown single crystals were formed by slow evaporation of  Ni  H₂L    Br₄ and Na₂ Fe CN  ₅ NO  · 2H₂O  molar ratio  1∶1  in water at room temperature. UV-vis  H₂O  $\lambda_{max}$  200  255  400 nm  IR ν  2176  2145  1937 cm⁻¹. Anal. calcd for NiFe₂C₂₂-H₄₂N₂₀O₆  C 30.97  H 4.96  N 32.84  found C 31.98 H 4.67  N 33.38.

*Complex* **3**     The same method for the preparation of complex **1** was adopted except the replacement of  Ni-

H₂L    ClO₄  ₄ by  Cu  H₂L    ClO₄  ₄  and red crystals were obtained. UV-vis  H₂O  $\lambda_{max}$  514 nm  IR  ν 2144  1924 cm⁻¹. Anal. calcd for CuFe₂C₂₂N₂₀H₄₂O₆  C 30.46  H 4.95  N 32.65  found C 30.80  H 4.95  N 32.07.

*Crystallographic data collection and structure determination*

Crystal data of complexes **1**  **2** and **3** were collected on a Rigaku R-Axis RIPID IP  a Bruker Smart CCD and a Bruker P4 diffractometer  respectively  with graphite-monochromated Mo Kα radiation. Intensity data were corrected for Lp effects and φ absorption correction. The structures were solved by direct method  SHELXS-97[17] and refined by full-matrix least-squares  SHELXL-97[18] on $F^2$. Hydrogen atoms were added geometrically and refined using a riding model. Crystal data of complexes **1**  **2** and **3** are presented in Table 2. CCDC-196870-196872 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www. ccdc.cam.ac.uk/conts/retrieving.html  or from the Cambridge crystallographic Data Centre  12  Union Road  Cambridge CB2 1EZ  UK  Fax    + 44 1223-336-033  or deposit@ccdc.cam.ac.uk  .

**Table 2**   Crystal data for **1**  **2** and **3**

| Crystal data | **1** | **2** | **3** |
|---|---|---|---|
| Empirical formula | NiFe₂C₂₂H₄₆N₂₀O₈ | NiFe₂C₂₂H₄₂N₂₀O₆ | CuFe₂C₂₂H₄₂N₂₀O₆ |
| Formula weight | 889.2 | 853.17 | 858 |
| Temperature  K | 123 2 | 293 2 | 293 2 |
| Measurement device | Rigaku R-Axis RIPID IP | Bruker Smart CCD | Bruker P4 |
| Wavelength  nm | 0.071073 | 0.071073 | 0.071073 |
| Crystal system | Triclinic | Monoclinic | Monoclinic |
| Space group | $P\bar{1}$ | $P2_1/n$ | $P2_1/n$ |
| $a$  nm | 1.0464 2 | 1.0354 2 | 1.0499 2 |
| $b$  nm | 1.0581 2 | 1.0828 2 | 1.0996 2 |
| $c$  nm | 0.9788 2 | 1.6292 3 | 1.5839 3 |
| $\alpha$  ° | 95.02 3 | | |
| $\beta$  ° | 76.12 3 | 96.06 3 | 94.396 12 |
| $\gamma$  ° | 109.03 3 | | |
| Volume  nm³ | 0.9945 3 | 1.8163 6 | 1.8232 6 |
| $Z$ | 1 | 2 | 2 |
| $D_c$  Mg/m³ | 1.485 | 1.56 | 1.563 |
| $F$  000 | 462 | 884 | 886 |
| $\mu$  mm⁻¹ | 1.225 | 1.367 | 1.429 |
| Reflections collected/unique | 3922/3922 | 16784/6677 | 4187/3203 |
| Reflections with $I > 2\sigma$  I | 1836 | 5022 | 2755 |
| Goodness-of-fit on $F^2$ | 0.894 | 1.025 | 0.973 |
| $R_1$  $I > 2\sigma$  I | 0.0704 | 0.0535 | 0.0388 |
| $wR_2$  all data | 0.1489 | 0.1485 | 0.0829 |

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