

Directed syntheses and structural studies of mononuclear copper(II) and heterodinuclear copper(II)–iron(III) complexes from the same unsymmetrical dinucleating ligand ‡

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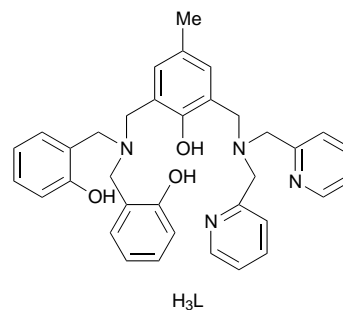
Mononuclear copper(II) [Cu(H₃L)(O₂CMe)]BPh₄ **1** and heterodinuclear copper(II)–iron(III) [FeCuL(μOEt)]ClO₄ **2** complexes from the same dinucleating ligand H₃L have been prepared and isolated {H₃L = 2-[bis(2-hydroxybenzyl)aminomethyl]-4-methyl-6-[bis(2-pyridylmethyl)aminomethyl]phenol}. The crystal structure of the mononuclear complex **1** demonstrated the site-directed complexation with H₃L. For the heterodinuclear complex **2** the crystal structure reveals that the copper and iron atoms are bridged by the central phenoxo moiety and by an exogenous ethoxo group. In addition this structure showed that the iron atom is five-co-ordinated. Temperature-dependent magnetic susceptibility measurements revealed an antiferromagnetic interaction (*ca.* $J = -58.1 \text{ cm}^{-1}$) between the copper and iron atoms in **2**. Cyclic voltammograms in dichloromethane vs. Ag–AgNO₃ revealed a quasi-reversible redox behaviour for Cu^{II}–Cu^I in **1** and **2** ($E_{1/2} = -0.77$ and -0.74 V respectively). The reduction of Fe^{III} in **2** is irreversible with $E_{pc} = -1.69$ V. The Cu^IFe^{III} complex is thermodynamically stable towards comproportionation.

Dinuclear centres containing transition metals such as iron and copper have attracted great interest due to their relevance to biological systems. Although numerous dinuclear complexes from dinucleating ligands have been described to date, few of them are heterodinuclear. This is, in part, due to the symmetrical nature of the ligands in which the two co-ordination sites are equivalent. A limited number of synthetic dinucleating ligands provide two chemically distinct environments. They have been used to prepare homodinuclear complexes exhibiting distinct properties of the two metal centres.¹ Heterodinuclear complexes are important in investigating their physical properties which may serve, in some cases, as models for heterodimetallic metalloenzyme active sites. Our interest has been focused on copper–iron complexes. Few non-haem complexes involving dinucleating ligands have been described and characterized by X-ray diffraction.²

We present here a mononuclear copper(II) complex [Cu(H₃L)(O₂CMe)]BPh₄ **1** and a copper(II)–iron(III) complex [FeCuL(μ-OEt)]ClO₄ **2** from the compound H₃L which possesses two sets of ion-bridging groups:³ a hard set provided by the bis-(hydroxyphenyl)methylamino moiety and a softer set provided by the bis(2-pyridylmethyl)amino moiety. The unsymmetrical nature of this compound allows a site-directed synthesis of the heterodinuclear complex. The mononuclear complex **1** provides a well suited precursor for the introduction of a second metal into the other co-ordination site under mild conditions (Scheme 1).

Experimental

All chemicals were obtained from commercial sources and used as received. Compound H₃L was synthesized according to the published method.³



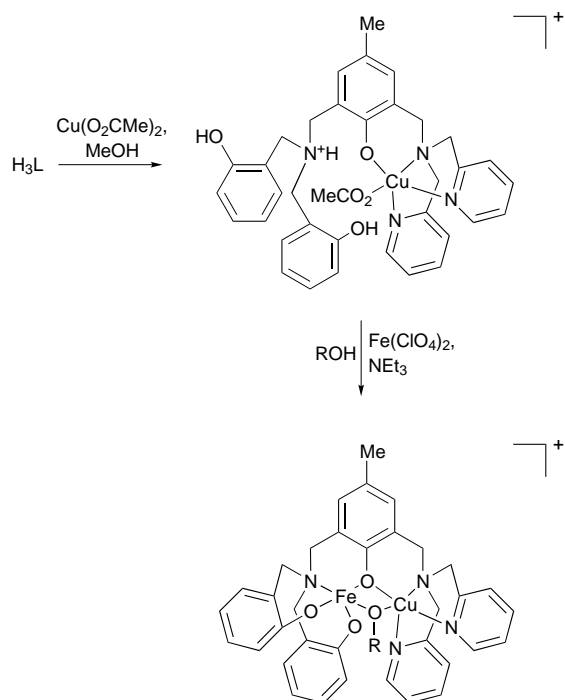
Elemental analyses were performed by the CNRS Micro-analysis Laboratory of Lyon, France. Magnetization data were collected on microcrystalline powders using a Quantum Design SQUID magnetometer over the temperature range 2–300 K, at 1 T field strength. Electronic spectra were obtained using a Uvikon 930 spectrometer with quartz cells. Electrochemical experiments were carried out using a PAR model 273 potentiostat equipped with a Kipp-Zonen *x-y* recorder, run under an argon atmosphere at room temperature, in dichloromethane (previously refluxed over CaH₂ and distilled under an argon atmosphere) with 0.1 mol dm⁻³ tetra-*n*-butylammonium perchlorate as supporting electrolyte. A Ag–0.01 mol dm⁻³ AgNO₃ reference electrode and a glassy carbon disc as working electrode (diameter: 5 mm) were used. A glassy carbon plate (2 × 2 cm) was employed for exhaustive electrolysis.

Preparations

[Cu(H₃L)(O₂CMe)]BPh₄ **1.** To a methanolic solution of H₃L (5 cm³, 0.089 mmol) was added 1 equivalent of Cu(O₂CMe)₂·H₂O in methanol (5 cm³). After 45 min, NaBPh₄ dissolved in methanol was added and the mixture was stirred for 45 min. Upon cooling, the precipitate was collected, dissolved in dichloromethane and vapour-phase diffusion of methanol in

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‡ Non-SI unit employed: $\mu_B \approx 9.27 \times 10^{-24} \text{ J T}^{-1}$.



Scheme 1 Stepwise complexation of $\text{Cu}(\text{O}_2\text{CMe})_2$ and $\text{Fe}(\text{ClO}_4)_3$ by unsymmetrical dinucleating ligand H_3L .

this solution afforded a blue crystalline material with a small amount of a brown product. The crystals were filtered off, washed with methanol and a small amount of dichloromethane to remove the brown impurities. Successive vapour-phase diffusion of methanol into the dichloromethane solution furnished crystals of complex **1** used for X-ray diffraction study (Found: C, 73.0; H, 5.9; Cu, 6.35; N, 5.6. Calc. for $\text{C}_{61}\text{H}_{59}\text{BCuN}_4\text{O}_5$: C, 72.95; H, 5.9; Cu, 6.2; N, 5.3%).

[FeCuL(μ -OEt)]ClO₄ **2.** To a methanolic solution of H_3L (5 cm³, 0.178 mmol) was added 1 equivalent of $\text{Cu}(\text{O}_2\text{CMe})_2 \cdot \text{H}_2\text{O}$ in methanol (4 cm³). The solution was stirred for 2 h and treated sequentially with 2.5 equivalents of triethylamine in methanol (2 cm³), 1 equivalent of $\text{Fe}(\text{ClO}_4)_3 \cdot 9\text{H}_2\text{O}$ in methanol (2 cm³), and 1 equivalent of NaOEt in methanol (2 cm³) leading to a solution which was stirred for 2 h. After cooling, the brown powder obtained was recrystallized from dichloromethane-ethanol to yield crystals of complex **2** used for the X-ray diffraction study (Found: C, 54.1; H, 4.7; Cl, 4.25; Cu, 7.25; Fe, 6.2; N, 6.65. Calc. for $\text{C}_{37}\text{H}_{38}\text{ClCuFeN}_4\text{O}_8$: C, 54.1; H, 4.65; Cl, 4.3; Cu, 7.7; Fe, 6.8; N, 6.8%).

CAUTION: although no problems were encountered during the preparation of the perchlorate salts, suitable care should be taken when handling such potentially hazardous compounds.

X-Ray crystallography

Crystals of compounds **1** and **2** were mounted on a Nicolet XRD four-circle diffractometer using a graphite-crystal monochromator [$\lambda(\text{Mo-K}\alpha) = 0.71073 \text{ \AA}$]. The temperature of measurement was 293 K. The reflections were corrected for Lorentz-polarization effects but not for absorption. The structures were solved using an automatic Patterson procedure with the SHELXS 86 program⁴ and refined against all F^2 (SHELXL 93).⁵

Crystal data for complex 1. $\text{C}_{61}\text{H}_{59}\text{BCuN}_4\text{O}_5$, $M = 1002.47$, blue platelet crystal $0.15 \times 0.25 \times 0.30 \text{ mm}$, monoclinic, space group $P2_1/n$, $a = 10.664(5)$, $b = 25.662(9)$, $c = 19.232(7) \text{ \AA}$, $\beta = 102.29(3)^\circ$, $U = 5167(4) \text{ \AA}^3$, $Z = 4$, $D_m = 1.289$, $D_c = 1.289 \text{ g cm}^{-3}$, $\mu = 0.477 \text{ mm}^{-1}$. 9418 Measured reflections in the range $3 \leq 2\theta \leq 50^\circ$; 8911 independent reflections. All non-hydrogen

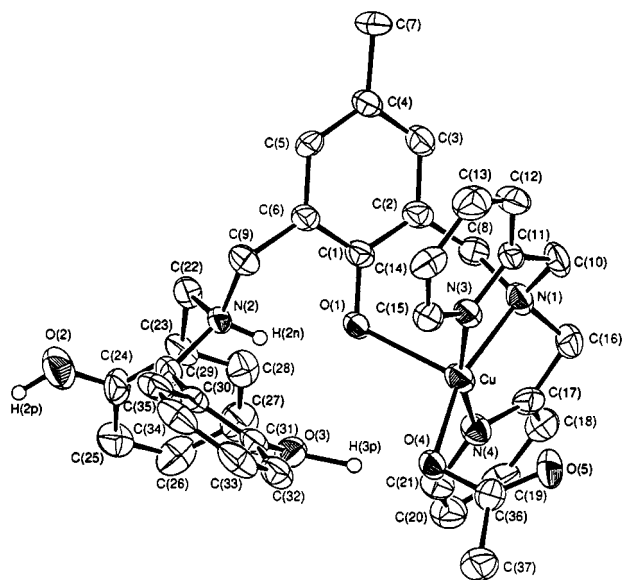


Fig. 1 Structure of the mononuclear cation of complex **1** in the crystal. Selected distances (\AA) and angles ($^\circ$): $\text{O}(3) \cdots \text{O}(4)$ 2.660(9), $\text{N}(2) \cdots \text{O}(1)$ 2.64(1), $\text{O}(2) \cdots \text{O}(5)$ 2.76(1), $\text{Cu}-\text{O}(1)$ 2.240(6), $\text{Cu}-\text{O}(4)$ 1.968(5), $\text{Cu}-\text{N}(1)$ 2.054(7), $\text{Cu}-\text{N}(3)$ 1.977(8), $\text{Cu}-\text{N}(4)$ 1.982(8) and $\text{N}(2)-\text{O}(1)$ 2.64(1); $\text{O}(4)-\text{Cu}-\text{O}(1)$ 105.9(2), $\text{O}(1)-\text{Cu}-\text{N}(3)$ 90.2(3), $\text{N}(3)-\text{Cu}-\text{N}(1)$ 83.3(3), $\text{N}(1)-\text{Cu}-\text{N}(4)$ 82.8(3) and $\text{N}(4)-\text{Cu}-\text{O}(4)$ 95.1(3)

atoms were refined with anisotropic thermal parameters. Hydrogen atoms of the ligand (except for ammonium and phenol hydrogen which were located on the Fourier-difference map and refined) and BPh_4^- counter ion were generated in idealized positions.

Crystal data for complex 2. $\text{C}_{37}\text{H}_{38}\text{ClCuFeN}_4\text{O}_8$, $M = 821.55$, dark platelet crystal $0.15 \times 0.20 \times 0.25 \text{ mm}$, monoclinic, space group $P2_1/c$, $a = 18.113(2)$, $b = 13.903(2)$, $c = 16.426(2) \text{ \AA}$, $\beta = 115.85(1)^\circ$, $U = 3723(1) \text{ \AA}^3$, $Z = 4$, $D_c = 1.466 \text{ g cm}^{-3}$, $\mu = 1.089 \text{ mm}^{-1}$. 7099 Measured reflections in the range $3 \leq 2\theta \leq 48^\circ$; 4146 independent reflections. All non-hydrogen atoms were refined with anisotropic thermal parameters. Three disordered oxygen atoms of the perchlorate anion were refined on two sites with a site occupation factor of 0.5. Hydrogen atoms of the ligand were generated in idealized positions and refined, riding on the carrier atoms, with isotropic thermal parameters $U(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for the methyl hydrogen atoms and $U(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for the aromatic hydrogen atoms. The final cycle of refinement including 496 parameters converged to $R(F) = 0.072$ [for 4146 $F > 4\sigma(F)$], $R(F^2) = 0.191$ for all 7099 F^2 ($\Delta\rho_{\text{max}} = 0.51$, $\Delta\rho_{\text{min}} = -0.54 \text{ e \AA}^{-3}$).

CCDC reference number 186/649.

Results and Discussion

Crystal structures

The crystal structure of complex **1** reveals a mononuclear species (Fig. 1). The copper is five-co-ordinated (square pyramidal) with three nitrogen atoms, one axial oxygen atom [O(1)] from the cresol moiety and one oxygen atom [O(4)] from the exogenous acetate group. The $\text{Cu}-\text{O}(1)$ distance is 2.240(6) \AA , the $\text{Cu}-\text{O}(4)$ distance 1.968(5) \AA and the $\text{Cu}-\text{N}$ distances range from 1.977(8) to 2.054(7) \AA . The two pyridine ligands are *trans* to each other. Furthermore the unco-ordinated nitrogen N(2) is protonated. Two intramolecular hydrogen bonds are observed: one between N(2)-H(2n) and O(1) and the other between O(3)-H(3p) of the phenol group and O(4) of the acetate ligand.

The crystal structure of complex **2** reveals a heterodinuclear $\text{Cu}^{\text{II}}\text{Fe}^{\text{III}}$ species (Fig. 2). The iron is five-co-ordinated to a

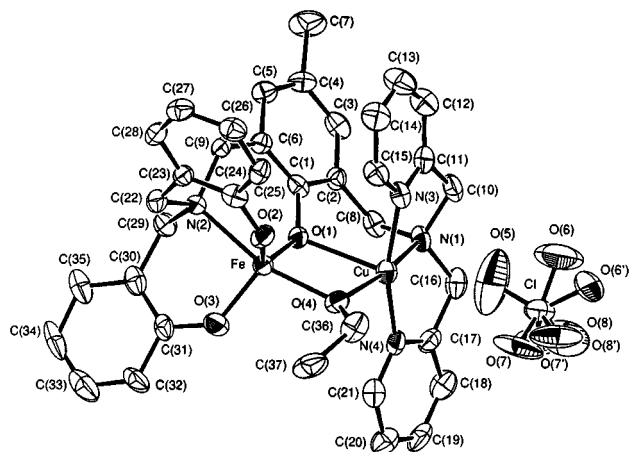


Fig. 2 Structure of the dinuclear complex **2** in the crystal. Selected distances (Å) and angles (°): Fe···Cu 3.122(2), Cu···O(5) 2.84(2), Cu–O(1) 2.322(6), Cu–O(4) 1.930(7), Cu–N(1) 2.012(8), Cu–N(3) 1.984(10), Cu–N(4) 1.956(9), Fe–O(1) 1.945(6), Fe–O(2) 1.847(8), Fe–O(3) 1.858(7), Fe–O(4) 1.971(6) and Fe–N(2) 2.184(8); Cu–O(1)–Fe 93.6(2), Cu–O(4)–Fe 106.3(3), O(1)–Fe–O(4) 83.8(3) and O(1)–Cu–O(4) 75.3(3)

nitrogen atom [N(2)] and four oxygen atoms: the two phenolate oxygens [O(2) and O(3)], a bridging oxygen from the cresol moiety and a bridging oxygen from an exogenous ethanolate ligand. An interaction is observed between an oxygen [O(5)] of the counter ion and the copper: O(5) is the only oxygen of ClO_4^- which is not disordered. Thus, the copper centre could be considered as octahedral. The elongation of 0.082 Å along the Cu–O(1) bond compared to Cu–O(1) in **1** evidences the Jahn–Teller distortion. The structure of **2** is very similar to the structure of the iron(III) complex $[\text{Fe}_2\text{L}(\mu\text{-OMe})(\text{OMe})]\text{BPh}_4$.^{1k} In **2** the phenoxo and the ethoxo bridges are non-symmetric and exhibited a shorter Fe···Cu [3.122(2) Å] distance compared to a reported $\text{Cu}^{\text{II}}\text{Fe}^{\text{III}}$ complex.^{2b} It has been emphasized that the complexation with a second metal atom (*i.e.* Fe^{III} from **1**) requires a major conformational change only around the C(22)–C(23) bond. This may be regarded as a minor structural reorganization.

Magnetic properties

Magnetic susceptibility studies of microcrystalline powders clearly indicate that the two metal ions of the dinuclear unit are antiferromagnetically coupled. The temperature dependence of the effective magnetic moment is shown in Fig. 3. The moment decreases from room temperature to 35 K. Between 35 and 15 K, a plateau is observed, indicating a Curie-law behaviour with a constant value of the magnetic moment equal to $4.4 \mu_{\text{B}}$. This confirms that the $S=2$ state is the ground state and that the $S=3$ state is no longer populated below 35 K, both $S=2$ and 3 states arising from coupling of the two spin states $S_{\text{Fe}} = \frac{5}{2}$ and $S_{\text{Cu}} = \frac{1}{2}$. Zero-field splitting of the $S=2$ state leads to further decrease of the magnetic moment when cooling to 2 K. The spin Hamiltonian (1) and the derived expression of the Zeeman

$$H = -JS_{\text{Fe}}S_{\text{Cu}} + D_{(S=2)}(S_z^2 - \frac{1}{3}S^2) + g\beta HS \quad (1)$$

energy levels were used in order to simulate the experimental data, the parameters J , D , and g having their usual meanings. The best fit of the theoretical values to the experimental data is shown as a solid line in Fig. 3. The following values of the spin-Hamiltonian parameters have been obtained: $J = -58.1 \text{ cm}^{-1}$, $D_{(S=2)} = 0.39 \text{ cm}^{-1}$, $g = 1.85$. This antiferromagnetic exchange interaction is comparable to those found in similar complexes formed from dinucleating ligands.^{2b}

Electronic spectra

The electronic spectrum of complex **1** in acetonitrile displays

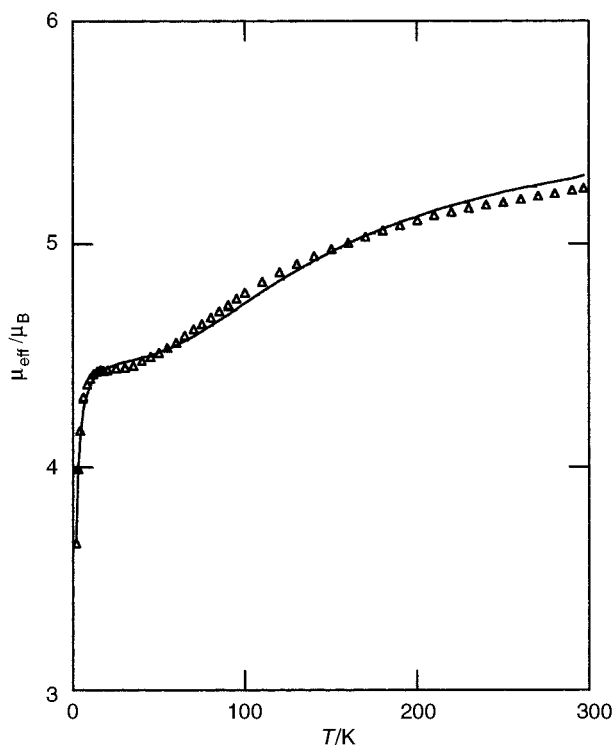


Fig. 3 Temperature dependence of the effective magnetic moments μ_{eff} is calculated as $2.828 (\chi_m T)^{1/2}$. The solid line represents the best fit of the theoretical susceptibility values to the experimental data

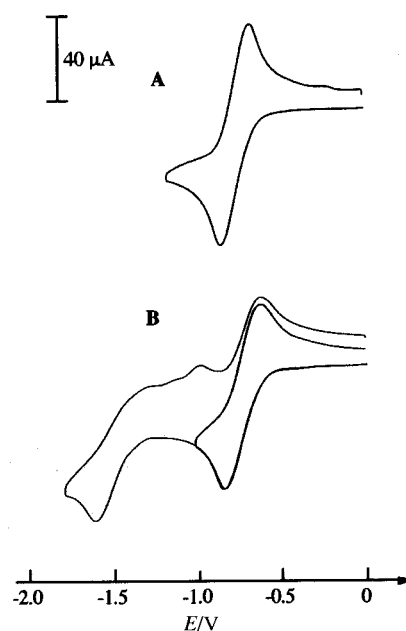


Fig. 4 The electrochemical behaviour of complexes **1** and **2** in $\text{CH}_2\text{Cl}_2 + \text{NBu}_4\text{ClO}_4$ (0.1 mol dm^{-3}) using a Ag–0.01 mol dm^{-3} AgNO_3 reference electrode and a glassy carbon disc as working electrode (diameter: 5 mm). Curves: A, a 2.3 mmol dm^{-3} solution of **1**; B, a 2.2 mmol dm^{-3} solution of **2**, $v = 0.1 \text{ V s}^{-1}$

main features at 444 ($\epsilon = 1091$) and 690 nm ($\epsilon = 276 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$). The band at 444 nm may be assigned to a phenolate to copper(II)⁶ charge-transfer transition (LMCT), and that of 690 nm to a d–d transition. Two bands are observed for **2** at 320 (sh) and 418 nm ($\epsilon = 5374 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$). That at 418 nm arises probably from the overlapping of the LMCT transitions from the phenolate ligands to Fe^{III} and Cu^{II} .

Electrochemistry

The cyclic voltammogram of complex **1** (Fig. 4, curve A) displays a quasi-reversible wave at $E_{1/2} = -0.77 \text{ V}$ ($\Delta E_p = 0.18 \text{ V}$,

$v = 0.1 \text{ V s}^{-1}$) which corresponds to the $\text{Cu}^{\text{II}}-\text{Cu}^{\text{I}}$ redox couple. Coulometric reduction confirms that it is a one-electron process. Further reduction occurs at $E_{\text{pc}} = -1.85 \text{ V}$ and leads to decomposition of the complex and deposition of Cu^0 onto the electrode surface.

The heterodimetallic complex **2** exhibits two electrochemical responses (Fig. 4, curve B) at -0.74 V ($\Delta E_{\text{p}} = 0.11 \text{ V}$, $v = 0.1 \text{ V s}^{-1}$) and $E_{\text{pc}} = -1.69 \text{ V}$ ($E_{\text{pa}} = -1.01 \text{ V}$, $v = 0.1 \text{ V s}^{-1}$) respectively. The first appears quasi-reversible. Exhaustive potentiostatic electrolysis at -0.9 V gives a $n = 1$ reduction process and reoxidation of this solution fully restores the initial solution as judged by UV/VIS and electrochemical measurements. We ascribe the first one-electron transfer to the $\text{Cu}^{\text{II}}-\text{Cu}^{\text{I}}$ redox couple. This assignment is consistent with redox potential values for $\text{Cu}^{\text{II}}-\text{Cu}^{\text{I}}$ in related complexes. In addition, the $\text{Cu}^{\text{II}}-\text{Cu}^{\text{I}}$ redox potentials for **1** and **2** are similar. The second electrochemical process leads to an iron(II) species. The voltammogram of the $[\text{Fe}_2\text{L}(\mu\text{-OMe})(\text{OMe})]\text{BPh}_4$ complex^{1k} showed for the second reduction process of the $\text{Fe}^{\text{III}}-\text{Fe}^{\text{II}}$ couple associated with the five-co-ordinated iron bonded to two phenolate terminal groups a shift to more cathodic potentials ($E_{\text{pc}} = -1.34 \text{ V}$ in CH_2Cl_2) compared to the iron bonded to two pyridyl groups ($E_{\text{c}} = -0.35 \text{ V}$ in CH_2Cl_2). The cathodic process leading to the $\text{Cu}^{\text{I}}\text{Fe}^{\text{II}}$ species seems to be associated with reorganization of the co-ordination sphere around the metal since the second electron transfer, centred on the iron atom, did not appear electrochemically reversible ($\Delta E_{\text{p}} = 0.68 \text{ V}$). The stability of the $\text{Cu}^{\text{I}}\text{Fe}^{\text{III}}$ form of **2** towards comproportionation can be evaluated by the corresponding constant k [$\Delta E_{\text{c}} = (RT/F)\ln k$]. From the separation of redox potentials ($\Delta E_{\text{c}} = 0.61$) we have determined k to be 1.48×10^{10} indicating that **2** has a stable $\text{Cu}^{\text{I}}\text{Fe}^{\text{III}}$ form.

Conclusion

The use of an unsymmetrical dinucleating ligand has allowed the synthesis of an heterodinuclear $\text{Cu}^{\text{I}}\text{Fe}^{\text{III}}$ complex. The copper has been placed first in the 'nitrogen box'. The crystal structure of the mononuclear copper complex has evidenced that the 'oxygen box' remained free for the complexation of another metal atom. In a second step, an Fe^{III} has been placed in the 'oxygen box'. The regiocontrolled syntheses of mono- and heterodi-nuclear complexes of the dinucleating ligand H_3L

have thus been evidenced. The compound H_3L had been designed with two sets of ion-binding groups suited to selective complexation. This strategy may be extended to the preparation of other heterodimetallic complexes with the view of avoiding a statistical distribution. Such complexes are relevant to the development of models for the active sites of dinuclear metalloproteins.

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