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FULL PAPER

Heterodimetallic copper(II) compounds containing ferrocenecarboxylato(−1) and triamines as ligands

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The syntheses and characterization of two new copper(II) complexes $[Cu(petdien)\{\eta^2\text{-}O_2C[(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)]\}][BPh_4]$ **1** and $[Cu(pmdien)(H_2O)\{\eta^1\text{-}O_2C[(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)]\}](ClO_4)$ **2** (petdien = *N*,*N*,*N*′,*N*″,*N*″-pentaethyldiethylenetriamine, pmdien = *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine) are reported. The structures of both compounds have been determined by X-ray diffraction and reveal that these complexes contain a heterodinuclear Cu(II)–Fe(II) cation in which the ferrocenecarboxylato(−1) ligand acts as a chelating agent in **1** or as a monodentate group in **2**. The influence of the steric effects induced by the tridentate amines in the mode of binding of the ferrocenecarboxylato group is discussed. Magnetochemical studies of these compounds are also reported.

Introduction

The study of heteropolynuclear organometallic compounds has attracted great interest in the past decade. One of the methods used to prepare heteropolymetallic compounds is based on the choice of ferrocenyl substrates containing heteroatoms (mainly nitrogen, sulfur, phosphorus or oxygen) and/or unsaturated groups with good donor abilities, which may allow the coordination of one or more metal ions.[1–10] In these types of materials, the presence of proximal metals in different environments, oxidation numbers and spin states may influence their mutual cooperation in a great number of different processes.[11–16] In addition, the interest in this sort of compound has increased considerably due to their outstanding properties and applications in a wide variety of areas.[17–25]

The synthesis and characterization of transition metal complexes containing ferrocenecarboxylato(−1) ligand appear to be especially interesting, since depending on the mode of coordination of this group to one or more metal cations, it may lead to a wide variety of interesting compounds, *i.e.* heterodi-, heterotri- or in general heteropoly-nuclear compounds.

On the other hand, copper(II) carboxylato complexes containing N-donor ligands as blocking groups have been widely studied in the past. For these systems it is well known that the presence of tridentate amines induces pentacoordination around the metal.[26,27] The geometry of the copper(II) varies from square-pyramidal (*SPY*) to trigonal bipyramidal (*TBPY*) depending on the presence of N-substituents in the blocking triamines.

Despite the two facts mentioned above, copper(II) complexes containing ferrocenecarboxylato(−1) ligands are scarce.[28–32] To the best of our knowledge only in one such case the copper(II) ion is bound to a tridentate amine.[32]

In this contribution, we present the syntheses and characterization of two novel copper(II) complexes containing simultaneously a neutral terdentate donor group {*N*,*N*,*N*′,*N*″,*N*″-pentaethyldiethylenetriamine (petdien) or *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (pmdien)} as blocking ligand and ferrocenecarboxylato(−1). In each one of these compounds the carboxylate group exhibits a different mode of binding, which could be explained in terms of the steric effects induced by the substituents on the N atoms of the triamines.

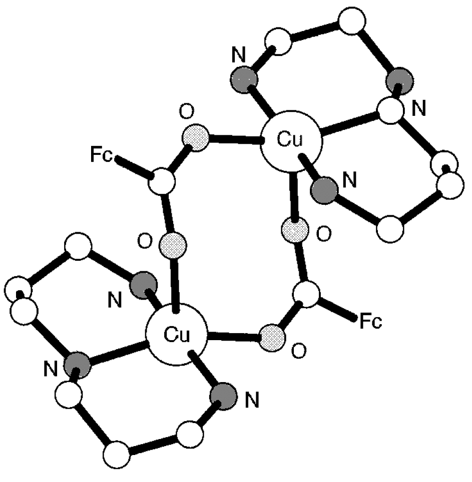

Fig. 1 Schematic representation of the dinuclear cation of $[Cu_2(dpt)_2\{\mu\text{-}O_2C[(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)]\}_2](ClO_4)_2$ **3**. Fc represents the $[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)]$ moiety.

Results and discussion

Our recent work with ferrocenecarboxylato–copper(II) complexes allowed the syntheses and characterization of $[Cu_2(dpt)_2\{\eta\text{-}O_2C[(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)]\}_2](ClO_4)_2$ **3** (dpt = dipropylenetriamine) in which two carboxylate groups act as bidentate bridging ligands (Fig. 1).[32] These findings suggested that since tridentate amines induce pentacoordination around the copper(II), the ferrocenecarboxylato ligands would tend to

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Table 1 Selected bond lengths (Å) and angles (°) for [Cu(petdien)-$\{\eta^2$-$O_2C[(\eta^5$-$C_5H_4)Fe(\eta^5$-$C_5H_5)]\}][BPh_4]$ **1**. Standard deviation parameters are given in parentheses

Cu(1)–O(1)	1.922(5)	Cu(1)–O(2)	2.489(5)
Cu(1)–N(1)	2.070(6)	Cu(1)–N(2)	1.994(7)
Cu(1)–N(3)	2.090(6)	O(1)–C(1)	1.288(9)
O(2)–C(1)	1.240(9)	C(1)–C(2)	1.469(10)
Fe(1)–C_{ring}[a]	2.012(18)	C_{ring}–C_{ring}[a]	1.401(15)
N(1)–Cu(1)–N(2)	85.6(3)	N(1)–Cu(1)–N(3)	153.0(3)
N(2)–Cu(1)–N(3)	87.9(3)	N(1)–Cu(1)–O(1)	95.4(2)
N(1)–Cu(1)–O(2)	101.4(2)	N(2)–Cu(1)–O(1)	167.6(2)
N(2)–Cu(1)–O(2)	109.5(2)	N(3)–Cu(1)–O(1)	96.5(2)
N(3)–Cu(1)–O(2)	105.5(2)	O(1)–Cu(1)–O(2)	58.18(19)
Cu(1)–O(1)–C(1)	102.5(4)	Cu(1)–O(2)–C(1)	77.8(4)
O(1)–C(1)–O(2)	121.0(7)	O(1)–C(1)–C(2)	116.5(7)
O(2)–C(1)–C(2)	122.3(7)		

[a] Average value for the ferrocenyl moiety.

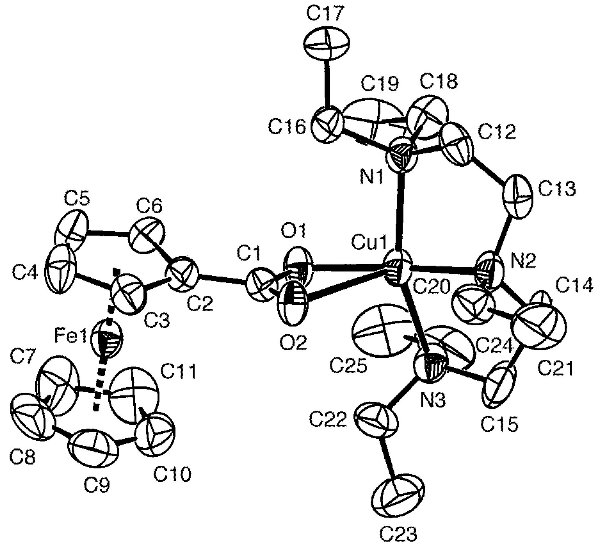

Fig. 2 Drawing of the cationic part of [Cu(petdien)$\{\eta^2$-$O_2C[(\eta^5$-$C_5H_4)Fe(\eta^5$-$C_5H_5)]\}][BPh_4]$ **1** with the atom labelling scheme.

occupy the two remaining coordination sites leading to polynuclear systems. In addition, changes in the nature of the substituents in the environment of the N-donor atoms of the amine ligands may also be important in modifying the coordination geometry of the Cu(II) ion and the mode of binding of the carboxylato group, allowing the control of superexchange interactions between the paramagnetic centres.[33,34] Nevertheless, the steric effect produced by the bulk of the ferrocenyl moieties can affect these trends. Taking into account these facts, we decided to study whether small changes on the tridentate alkylic N-donor ligands in the coordination sphere of the copper(II) could be important to modify the mode of binding of the ferrocenecarboxylato(−1) group to the metal and the structures of these compounds. These factors may affect the magnetochemical properties of this type of compound.

Crystal structures

[Cu(petdien)$\{\eta^2$-$O_2C[(\eta^5$-$C_5H_4)Fe(\eta^5$-$C_5H_5)]\}][BPh_4]$ 1. Compound **1** crystallizes as an ionic array of [Cu(petdien)-$\{\eta^2$-$O_2C[(\eta^5$-$C_5H_4)Fe(\eta^5$-$C_5H_5)]\}]^+$ cations and tetraphenylborate anions. The structure of the cationic moiety together with the atomic numbering scheme are presented in Fig. 2. Selected bond distances and angles are listed in Table 1.

The central copper(II) atom, Cu(1), is bound to three nitrogen atoms N(1), N(2) and N(3) of the triamine and the two oxygen atoms O(1) and O(2) of the ferrocenecarboxylato(−1) anion. The carboxylate binds to the metal in an η^2-mode, thus yielding an asymmetric stretched four-membered chelate, with two different Cu–O bond lengths [Cu(1)–O(1) 1.922(5) Å and Cu(1)–O(2) 2.489(5) Å], a bite angle of 121.0(7)° and a O(1)–Cu(1)–O(2) angle of 58.18(19)°. The fact that the ferrocenyl moiety and the ethyl N-substituents lie away from each other led us to assume that their steric hindrance prevents the ferrocenecarboxylato to act as a bridge.

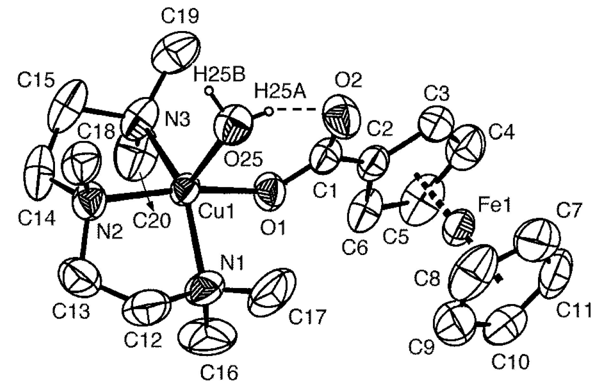

Fig. 3 Molecular structure and atom labelling scheme of the cation of [Cu(pmdien)$(H_2O)\{\eta^1$-$O_2C[(\eta^5$-$C_5H_4)Fe(\eta^5$-$C_5H_5)]\}](ClO_4)$ **2**.

Although the long Cu(1)–O(2) distance suggests a square-pyramidal 4 + 1 coordination, the basal atoms fall more than 0.3 Å away from their least-squares plane, thus indicating a strong distortion. The study of the five-coordination points to a geometry which is intermediate between square-pyramidal (*SPY*) and trigonal bipyramidal (*TBPY*). Holmes' analysis[35] of the dihedral angles gives 55% Berry pseudorotation from *SPY* to *TPBY* fixing O(2) as the pivot atom. This result is confirmed by an Addison's τ parameter[36] of 0.25 (this is 0.00 and 1.00 for idealized *SPY* and *TBPY* geometries, respectively). Despite the fact that the presence of bulky ethyl N-substituents in the complexing amine should induce a higher degree of *TBPY* character,[37–40] the formation of the chelate ring forces a narrow O(1)–Cu(2)–O(2) angle, thus resulting in a decrease of the axial *TBPY* angle and an increase of the equatorial N(1)–Cu(1)–N(3) angle [153.0(3)°]. A similar type of distortion has also been reported for related copper(II) compounds containing Cu^{II}(petdien)(O_2CR-*O*,*O′*) coordination environments.[38–40]

Concerning the ferrocenyl moiety, the Fe–C ring and the C–C ring bond lengths and angles in **1** are consistent with those reported in the literature.[41] The carboxylate group is not coplanar with the C_5H_4 ring, forming a 14.0° dihedral angle. The pentagonal Cp rings are nearly parallel (tilt angle = 0.6°) and their relative orientation deviates by 10.3° from the eclipsed conformation. Direct interaction between the Cu and Fe atoms is ruled out as they are 5.512 Å apart.

[Cu(pmdien)$(H_2O)\{\eta^1$-$O_2C[(\eta^5$-$C_5H_4)Fe(\eta^5$-$C_5H_5)]\}](ClO_4)$ 2. The crystal structure of **2** consists of perchlorate anions and [Cu(pmdien)$(H_2O)\{\eta^1$-$O_2C[(\eta^5$-$C_5H_4)Fe(\eta^5$-$C_5H_5)]\}]^+$ cations. The structure of the cationic moiety and the atomic numbering scheme are depicted in Fig. 3. Selected bond distances and angles are presented in Table 2.

Within the cation, the copper ion is bonded to the three nitrogen atoms of the triamine [N(1), N(2) and N(3)] and to the O(1) of the ferrocenecarboxylate anion at 1.940(3) Å, which exhibits the typical features of an η^1-O_2CR coordination in a *syn* orientation. The pentacoordination around the Cu(II) ion is completed by binding the oxygen atom O(25) of a water molecule at 2.245(3) Å. The metal geometry is again intermediate between *SPY* and *TBPY*, although closer to *SPY* than in **1**, as a result of the smaller bulk of the groups on the N-donor atoms: the Addison's parameter[36] is slightly lower (τ = 0.24) and the Holmes' pseudorotation coordinate,[35] taking O(25) as pivot atom, is reduced to 20%. The latter result is reflected in the fact that O(1), N(1), N(2) and N(3) are less than 0.13 Å from their

Table 2 Selected bond lengths (Å) and angles (°) for [Cu(pmdien)(H_2O){η^1-O_2C[(η^5-C_5H_4)Fe(η^5-C_5H_5)]}](ClO_4) **2**. Standard deviation parameters are given in parentheses

Cu(1)–O(1)	1.940(3)	Cu(1)–O(25)	2.245(3)
Cu(1)–N(1)	2.057(4)	Cu(1)–N(2)	2.035(4)
Cu(1)–N(3)	2.052(4)	O(2)–O(25)	2.637(5)
O(1)–C(1)	1.277(5)	O(2)–C(1)	1.239(5)
C(1)–C(2)	1.482(6)	Fe(1)–C_{ring}[a]	2.036(9)
C_{ring}–C_{ring}[a]	1.404(20)		
N(1)–Cu(1)–N(2)	85.82(17)	N(1)–Cu(1)–N(3)	153.71(18)
N(2)–Cu(1)–N(3)	86.51(17)	N(1)–Cu(1)–O(1)	90.69(15)
N(1)–Cu(1)–O(25)	100.57(16)	N(2)–Cu(1)–O(1)	168.14(14)
N(2)–Cu(1)–O(25)	98.83(14)	N(3)–Cu(1)–O(1)	91.70(15)
N(3)–Cu(1)–O(25)	105.45(15)	O(1)–Cu(1)–O(25)	92.95(13)
Cu(1)–O(1)–C(1)	130.8(3)	O(2)–C(1)–O(1)	125.9(4)
O(1)–C(1)–C(2)	114.4(4)	O(2)–C(1)–C(2)	119.7(4)

[a] Average value for the ferrocenyl moiety.

least-squares plane, while the Cu(1) is 0.33 Å towards the apical position. A special feature of the cation arises from the relative arrangement between the free oxygen atom of the carboxylate O(2) and the coordinated water molecule, which leads to an O(2) $\cdots$ O(25) distance of 2.637(5) Å. The determined position of H(25A), at 0.82(4) Å from O(25) and 1.87(4) Å from O(2) clearly indicates the presence of an intramolecular hydrogen bond, forming an O–H $\cdots$ O angle of 155(5)°. This interaction contributes to a further stabilization of the complex due to the formation of an aditional six-membered chelate ring around the copper(II) ion, where the six atoms are nearly coplanar (maximum deviation of 0.09 Å from their least-squares plane). Analogous H-bonding interactions have also been described for related mono- and di-nuclear copper(II) complexes containing pmdien, such as [Cu(pmdien)(H_2O)(η^1-O_2CMe)]$^+$ [42,43] or [{Cu(pmdien)(H_2O)}$_2$(μ-tp)]$^{2+}$ (tp = terephthalato),[40] and in the structurally related complexes [{Cu(ettmdien)(H_2O)}$_2$(μ-CO_3-*O*,*O′*)]$^{2+}$ (ettmdien = *N′*-ethyl-*N*,*N*,*N″*,*N″*-tetramethyldiethylenetriamine),[44] [Cu(tmtacn)(H_2O)(η^1-O_2CMe)]$^+$,[45] and [{Cu(tmtacn)(H_2O)}$_2$(μ-tp)]$^{2+}$ (tmtacn = 1,4,7-trimethyl-1,4,7-triazacyclononane).[46] Bond lengths and angles involving the (η^5-C_5H_5)Fe(η^5-C_5H_4) unit in **2** are consistent with those reported in the literature for other ferrocene derivatives.[41] The pentagonal rings of the ferrocenyl fragment are planar and nearly parallel (tilt angle: 1.2°) and they deviate from the eclipsed conformation by 11.1°. The bite angle of the carboxylate group is 125.9(4)° and the dihedral angle that forms with the C_5H_4 bound ring is 6.7°. The distance between Cu(1) and Fe(1) [5.723(3) Å] is greater than in **1**.

Spectroscopic and magnetochemical studies

Compounds **1** and **2** were characterized by FAB+ mass spectrometry in CH_2Cl_2 solution. For **1** the peak corresponding to the [Cu(petdien){η^2-O_2C[(η^5-C_5H_4)Fe(η^5-C_5H_5)]}]$^+$ cation was observed at *m*/*z* 535. In contrast, the spectrum of **2** in the same conditions suggested the loss of the water molecule coordinated to the copper atom (*m*/*z* 465, which is in accord with the presence of the cation [Cu(pmdien){η^2-O_2C[(η^5-C_5H_4)Fe(η^5-C_5H_5)]}]$^+$). This fact points to a modification of the coordination sphere of the copper(II) ion when **2** is poured in solution.

In the infrared spectra of these compounds, the bands due to the asymmetric stretchings of the carboxylato group $\nu(CO_2)$ appeared at 1561 cm^{-1}, and that of symmetric stretchings at 1384 cm^{-1} for **1** and at 1330 cm^{-1} for **2**. The position of these bands as well as their separation, $\Delta\nu$, are similar to those reported for [Cu(L)$_2${η^2-O_2C[(η^5-C_5H_4)Fe(η^5-C_5H_5)]}$_2$] (with L = pyridine or imidazole)[29] suggesting an asymmetrical bidentate coordination mode of the carboxylate moiety.[28,29]

The UV–VIS spectra of 10^{-3} M solutions of compounds **1** and **2** in CH_2Cl_2 showed a band centered at *ca.* 455 nm and an additional absorption at 650 nm (for **1**) and at 648 nm (for **2**). The higher energy band is typical of the ferrocenyl moiety and occurs at 460 nm for the free ferrocenecarboxylic acid. The small shift in its position upon complexation suggests that the binding of the "Cu(triamine)" unit does not produce a significant modification of the electronic structure of the ferrocenyl fragment. This finding has also been reported for related Cu(II) systems.[28,29] The other bands in the range 630–660 nm are assigned to the copper d–d transitions, the position of which is consistent with the values reported for the mononuclear Cu(II) complexes [Cu(pmdien)Cl_2] and [Cu(petdien)Cl_2].[47]

Susceptibility measurements in microcrystalline samples of compound **1** show a paramagnetic behaviour with a constant $\chi_M T$ value of 0.44 cm^3 K mol^{-1}, corresponding to an uncoupled ($S_{Fe(II)} = 0$, $S_{Cu(II)} = 1/2$) system. The EPR spectra of both powder and frozen CH_2Cl_2 solution samples are temperature-independent and consist of an axial pattern with a poorly resolved hyperfine structure due to the coupling with the copper nucleus ($g_{\parallel} = 2.08$, $g_{\perp} = 2.21$ and $A_{\perp} = 177$ G).

The powder EPR spectrum of **2** exhibits a similar shape, but in this case the anisotropic *g* signals overlap, leading to an asymmetric broad band centered at 3361 G. No hyperfine splitting is distinguishable in the solid sample. In the frozen solution, the band is centered at 3251 G and the hyperfine signals were feebly resolved ($A = 193$ G); as mentioned above, a change in the coordination sphere of Cu(II) is likely to occur in these conditions. The paramagnetic susceptibility of powdered sample of **2** gives a $\chi_M T$ value of 0.42 cm^3 K mol^{-1}, which points to a g_{iso} of 2.11.

Conclusions

As expected in the compounds under study, the complexation with triamines induces pentacoordination around the copper(II) ion. In all cases, three coordination sites are occupied by the nitrogen atoms of the amine. In addition, the metal binds tightly to one of the oxygen atoms of the ferrocenecarboxylato ligand, O(1), which lies on one of the vacant sites. The occupancy of the fifth position, which determines the mode of coordination of the carboxylato ligand, is governed by two factors: the basicity of the second O-donor of the ferrocenecarboxylato, O(2), and the steric effects induced by the substituents on the N-donor atoms of the triamines. Regarding the first factor, a general survey of structurally characterized metal–carboxylate complexes[48] has shown that *syn*-binding of the O_2CR groups is the most commonly encountered carboxylate binding mode (*i.e.* as monodentate terminal, chelating or bidentate bridging ligands). This fact has been explained on the basis of the greater basicity of the *syn* lone pairs of the oxygen atoms when compared with their *anti* lone pairs. This allows the binding of the O(2) to an acceptor which is chosen by the proximity to their *syn* lone pair: Cu(1) in **1**, H(25A) in **2** or another Cu(II) ion as in the binuclear compound [Cu_2(dpt)$_2${μ-O_2C-[(η^5-C_5H_4)Fe(η^5-C_5H_5)]}$_2$](ClO_4)$_2$ **3**.[32] In the three cases, the ferrocenecarboxylato group exhibits a *syn*,*syn*-binding.

The differences observed in the mode of coordination of the carboxylate group in compounds **1**–**3** can be related to the steric effects produced by the bulk of the substituents on the N-donor atoms of the triamines, which modify the geometry of the coordination sphere of the copper(II) ion. In **1**, once the ferrocenecarboxylato binds through O(1) to the [Cu(petdien)]$^{2+}$ moiety, the environment around the metal becomes so crowded that it hinders the incorporation of an external donor group in the remaining coordination site. Thus the possibilities of the metal to fulfil the pentacoordination are limited to a weak bond with the nearby and *syn*-oriented O(2) of the carboxylate group, leading to an assymmetric η^2-chelate.

For compound **2** the effective bulk of the terminal methyl groups of pmdien is smaller than the terminal ethyl groups in **1**, as reflected in Charton's steric parameters (ES-CH) for the two groups: 5.00 for NEt_2 and 3.00 for NMe_2.[49] In addition, the

Table 3 Crystal data and structure refinement details for compounds **1** and **2**. Standard deviation parameters are given in parentheses

	1	**2**
Chemical formula	$C_{49}H_{62}BCuFeN_3O_2$	$C_{20}H_{34}ClCuFeN_3O_7$
Formula weight	855.22	583.34
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
a/Å	12.743(4)	11.271(2)
b/Å	14.115(5)	15.369(1)
c/Å	14.295(5)	15.852(7)
α/°	77.92(4)	90.0
β/°	68.16(3)	110.63(2)
γ/°	67.43(4)	90.0
V/Å^3	2197.2(13)	2569.9(12)
Z	2	4
T/K	293(2)	293(2)
μ(Mo-Kα)/mm^{-1}	0.856	1.539
No. of reflections collected	14016	9680
No. of reflections unique (R_{int})	10565 (0.0606)	8089 (0.0234)
No. of reflections observed	4242	3433
$R1$, $wR2$ [$I > 2\sigma(I)$]	0.1083, 0.2806	0.0572, 0.1496
(all data)	0.2771, 0.3478	0.2028, 0.1764

triamine induces a higher degree of square-pyramidal geometry, which increases the accesibility of an external ligand (H_2O) to the apical position. For this distribution of ligands the relative orientation of one of the hydrogen atoms of the water molecule, H(25A), and the *syn* oriented O(2) atom is appropriate to permit intramolecular hydrogen bonding, leading to a nearly-planar six-membered chelate ring involving the ferrocenecarboxylato group.

In compound **3**, the terminal $-NR_2$ groups of dpt are less bulky than in the above two compounds (ES-CH = 1.00 for $-NH_2$).[49] Thus the free space available around the Cu(II) becomes larger than in **1**, and allows the approach of a second ferrocenecarboxylate ligand that forms a weak O(2′)–Cu(1) bond, which generates the core of the tetrametallic entity. The fact that the latter bond is established in the apical position of the *SPY* environment of the copper atoms results in orthogonality of the magnetic orbitals leading to a ferromagnetic interaction.

To summarise, the results reported here show not only the high versatility of the ferrocenecarboxylato ligand but also the importance of the nature of the substituents on the nitrogen atoms of the triamines in determining the nuclearity of the resulting complex: small substituents favour the formation of dimeric magnetically coupled systems (in **3**), whereas bulkier groups yield monomeric paramagnetic species (in **1** or **2**).

Experimental

Synthesis

Ferrocenecarboxylic acid, the amines (petdien and pmdien), $Cu(ClO_4)_2\cdot 6H_2O$ and $Na[BPh_4]$ were purchased from Aldrich and used as received. Sodium ferrocenecarboxylate was prepared as described previously.[50] The organic solvents used in this work (MeOH, CH_2Cl_2 and *n*-hexane) were HPLC grade.

CAUTION: perchlorate salts of metal complexes are potentially explosive. Only a small amount of material should be used and they should be handled with caution.

[Cu(petdien){η^2-O_2C[(η^5-C_5H_4)Fe(η^5-C_5H_5)]}][BPh_4] 1. A 370 mg (1 mmol) amount of $Cu(ClO_4)_2\cdot 6H_2O$ was dissolved in 10 cm^3 of methanol. Then a solution formed by 240 mg (1 mmol) of *N*,*N*,*N*′,*N*″,*N*″-pentaethyldiethylenetriamine in 5 cm^3 of methanol was added at room temperature and stirred for *ca.* 10 min. After this period, 250 mg of sodium ferrocenecarboxylate (1 mmol) in 10 cm^3 of methanol were added slowly under continuous stirring at room temperature, *ca.* 20 °C. The colour of the reaction mixture changed from blue to greenish. Once the addition had finished the mixture was stirred for 20 additional min at room temperature. Finally, addition of a solution containing 680 mg (2 mmol) of $NaBPh_4$ in 10 cm^3 of methanol led to the precipitation of a dark-bluish solid which was collected by filtration and air-dried. Blue-green needles of **1** were obtained by slow evaporation at *ca.* 4 °C of a CH_2Cl_2 solution of the complex layered with *n*-hexane. Further crystallizations were carried out; however, the quality of the crystals was not improved. The yield was 700 mg (82%) (C, 68.8; H, 7.4; N, 5.0. $C_{49}H_{62}N_3O_2BCuFe$ requires: C, 68.82; H, 7.31; N, 4.91%). FAB$^+$ MS: *m*/*z* 535, [Cu(petdien){η^2-O_2C[(η^5-C_5H_4)Fe(η^5-C_5H_5)]}]$^+$. ν_{max}/cm^{-1} 2975–3000 (C–H); 1561, 1475, 1384, 1335 (CO_2). λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) = 455 (323) and 650 (272).

[Cu(pmdien)(H_2O){η^1-O_2C[(η^5-C_5H_4)Fe(η^5-C_5H_5)]}](ClO_4) 2. A solution of $Cu(ClO_4)_2\cdot 6H_2O$ (370 mg, 1 mmol) was dissolved in 2 cm^3 of methanol. Then a solution formed by *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (174 mg, 1 mmol) and 5 cm^3 of methanol was added at room temperature. The resulting blue mixture was stirred for 5 min and after this period, a solution containing 250 mg (1 mmol) of sodium ferrocenecarboxylate and 10 cm^3 of methanol was added slowly under continuous stirring at room temperature (*ca.* 20 °C). The colour of the reaction mixture changed from blue to greenish. Once the addition was finished, the resulting solution was stirred for 20 additional min at room temperature. The undissolved materials were removed by filtration and discarded. Slow evaporation of the filtrate at room temperature produced deep-green crystals of **2**. The yield was 415 mg (75%) (C, 41.3; H, 5.8; N, 7.2. $C_{20}H_{33}N_3O_7ClCuFe$ requires: C, 41.25; H, 5.71; N, 7.22%). FAB$^+$ MS: *m*/*z* 465, [Cu(pmdien){η^2-O_2C[(η^5-C_5H_4)-Fe(η^5-C_5H_5)]}]$^+$. ν_{max}/cm^{-1}: 2950–2750 (C–H); 1561, 1471, 1380, 1344 (CO_2); 1122, 1105, 1064 (ClO_4^-). λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) = 455 (323) and 648 (257).

Physical measurements

Spectral and magnetic. FAB+ mass spectra were obtained with a VG-Quatro Fission Instrument using 3-nitrobenzyl-alcohol (NBA) as matrix. Infrared spectra were recorded in the range 4000–400 cm^{-1} with a Nicolet Impact 400 instrument using KBr pellets. UV–VIS spectra of 10^{-3} M solutions of compounds **1** and **2** in CH_2Cl_2 were recorded in the range 300–700 nm at room temperature with a Shimadzu-UV-160A instrument. The EPR spectra of microcrystalline samples of **1** and **2** as well as of the frozen CH_2Cl_2 solutions of these complexes were recorded at X-band frequency (9.78 GHz) with a Bruker ES-200 spectrometer in the temperature range 300–4 K. Susceptibility measurements were carried out in the range

300–4 on powdered samples of **1** and **2** with a Manics-DSM8 pendulum type magnetometer equipped with a Drusch-EAF-16UE electromagnet and helium continuous flow cryostat.

Crystal structure determination. Crystals of **1** (0.06 × 0.11 × 0.46 mm) and of **2** (0.06 × 0.34 × 0.52 mm) were selected and mounted on an Enraf-Nonius CAD4 four-circle diffractometer. Graphite monochromated Mo-Kα radiation ($\lambda = 0.710\,69$ Å) was used to collect the data set; the ω–2θ scan technique was employed. Unit cell parameters were determined from automatic centring of 15 reflections. Three reflections were measured every 2 h as orientation and intensity control. No significant intensity decay was observed for **2**, but was 16.2% for **1**, which was corrected using a polynomial fitting of the standards decay. Ψ-Scan absorption correction was applied. The crystallographic data, experimental conditions and some features of the structure refinement are listed in Table 3.

The structures were solved by direct methods and refined using full-matrix least squares on F^2. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at calculated positions using a riding model, except for H(25A) and H(25B) in **2**, which were located in the Fourier synthesis and their positions refined. In both structures, H-atoms were refined with a global isotropic thermal factor. All calculations were performed using the SHELX-97 package.[51]

CCDC reference numbers 160991 and 160992.

See http://www.rsc.org/suppdata/dt/b1/b102030g/ for crystallographic data in CIF or other electronic format.

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