Design, Synthesis, and Structural Characterization of Molecular and Supramolecular Heterobimetallic Metallamacrocycles Based on the 1,1′-Bis(4-pyridyl)ferrocene ($Fe(\eta^5\text{-}C_5H_4\text{-}1\text{-}C_5H_4N)_2$) Ligand

Dario Braga,* Marco Polito, Daniela D'Addario, and Emilio Tagliavini

Dipartimento di Chimica G. Ciamician, Università di Bologna,
Via Selmi 2, 40126 Bologna, Italy

Davide M. Proserpio

Dipartimento di Chimica Strutturale e Stereochimica Inorganica, Università di Milano,
Via Venezian 21, 20133 Milano, Italy

Fabrizia Grepioni*

Dipartimento di Chimica, Università di Sassari, Via Vienna 2, 07100 Sassari, Italy

Jonathan W. Steed

Department of Chemistry, King's College London, Strand, London WC2R 2LS, U.K.

Received June 4, 2003

The bidentate ferrocenyl sandwich $[Fe(\eta^5\text{-}C_5H_4\text{-}1\text{-}C_5H_4N)_2]$ (**1**) has been used as a coordination ligand in reactions with $AgNO_3$, $Cd(NO_3)_2$, $Cu(CH_3COO)_2$, $Zn(CH_3COO)_2$, and $ZnCl_2$ to obtain the heterobimetallic metallamacrocyclic derivatives $[Fe(\eta^5\text{-}C_5H_4\text{-}1\text{-}C_5H_4N)_2]_2Ag_2(NO_3)_2\cdot 1.5H_2O$, $[Fe(\eta^5\text{-}C_5H_4\text{-}1\text{-}C_5H_4N)_2]_2Cu_2(CH_3COO)_4\cdot 3H_2O$, $[Fe(\eta^5\text{-}C_5H_4\text{-}1\text{-}C_5H_4N)_2]_2Cd_2(NO_3)_4\cdot CH_3OH\cdot 0.5C_6H_6$, $[Fe(\eta^5\text{-}C_5H_4\text{-}1\text{-}C_5H_4N)_2]_2Zn_2(CH_3COO)_4$, and $[Fe(\eta^5\text{-}C_5H_4\text{-}1\text{-}C_5H_4N)_2]_2Zn_2Cl_4$ (abbreviated in the following as $(\mathbf{1}Ag^{I})_2^{2+}$, $(\mathbf{1}Cd^{II})_2^{4+}$, $(\mathbf{1}Cu^{II})_2^{4+}$, $(\mathbf{1}Zn^{II}_{acetate})_2^{4+}$, and $(\mathbf{1}Zn^{II}_{chloride})_2^{4+}$). The reaction with the ferrocenedicarboxylic acid complex $[Fe(\eta^5\text{-}C_5H_4\text{-}COOH)_2]$ has led to the supramolecular adduct $[Fe(\eta^5\text{-}C_5H_4\text{-}1\text{-}C_5H_4N)_2][Fe(\eta^5\text{-}C_5H_4COOH)_2]$ ($\mathbf{1}[Fe(\eta^5\text{-}C_5H_4COOH)_2]$). All compounds have been structurally characterized by single-crystal X-ray diffraction.

Introduction

There is great current interest in the possibility of using preformed organometallic complexes as ligands in the construction of mixed-metal superstructures.[1] A major issue of organometallic supramolecular chemistry is that of exploiting the topological, electronic, and spin properties of metal centers to construct molecular materials in which metal centers communicate via coordination bonds or other noncovalent interactions.[2] Joining metal atoms via ligands is at the core of the booming field of coordination network chemistry.[3,4]

We are interested in applying supramolecular chemistry approaches to organometallic chemistry, with a focus on crystal engineering strategies.[5]

In a previous paper of this series,[6] we have reported the synthesis and characterization of a family of mono- and bidentate pyridyl and pyrimidyl derivatives of the ferrocenediboronic acid complexes $[Fe(\eta^5\text{-}C_5H_4\text{-}B(OH)_2)_2]$. Among others we have synthesized the bis(pyridyl) complex $[Fe(\eta^5\text{-}C_5H_4\text{-}4\text{-}C_5H_4N)_2]$ as well as the bis(phenylpyridyl) complex $[Fe(\eta^5\text{-}C_5H_4\text{-}C_6H_4\text{-}4\text{-}C_5H_4N)_2]$ and the bis(pyrimidyne) complex $[Fe(\eta^5\text{-}C_5H_4\text{-}5\text{-}C_4H_3N_2)_2]$. We intended to exploit these bidentate compounds in the construction of supramolecular "complexes-of-complexes" whereby the N termini on the ferrocenyl unit could be used to coordinate to metal centers. A similar approach has been used before by others.[7,8] A second

---

* To whom correspondence should be addressed. E-mail: dbraga@ciam.unibo.it.

(1) (a) Haiduc, I.; Edelmann, F. T. *Supramolecular Organometallic Chemistry*; Wiley-VCH: Weinheim, Germany, 1999. (b) Steed, J. W.; Atwood, J. L. *Supramolecular Chemistry*; Wiley: New York, 2000.

(2) (a) Braga, D.; Grepioni, F. *Acc. Chem. Res.* **2000**, *33*, 601. (b) Garcia, A. M.; Bassani, D. M.; Lehn, J. M.; Baum, G.; Fenske, D. *Chem. Eur. J.* **1999**, *5*, 1234.

(3) See, for recent entries: (a) Eddaouddi, M.; Moler, D. B.; Li, H.; Chen, B.; Reineke, T. M.; O'Keeffe, M.; Yaghi, O. M. *Acc. Chem. Res.* **2001**, *34*, 319. (b) Batten, S. R. *CrystEngComm* **2001**, 28.

(4) (a) *J. Chem. Soc., Dalton Trans.* **2000**, 3705 (whole issue). (b) Moulton, B.; Zaworotko, M. J. *Chem. Rev.* **2001**, *101*, 1629. (c) Blake, A. J.; Champness, N. R.; Hubberstey, P.; Li, W. S.; Withersby, M. A.; Schroder, M. *Coord. Chem. Rev.* **1999**, *183*, 117 and references therein.

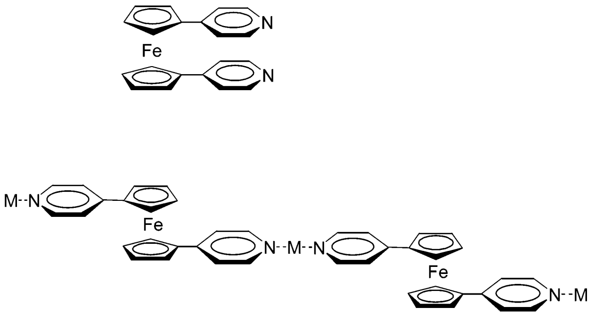
(5) (a) Braga, D.; Grepioni, F.; Desiraju, G. R. *Chem. Rev.* **1998**, *98*, 1375. (b) Braga, D.; Grepioni, F. *Coord. Chem. Rev.* **1999**, *183*, 19.

(6) Braga, D.; Polito, M.; Bracaccini, M.; D'Addario, D.; Tagliavini, E.; Sturba, L.; Grepioni, F. *Organometallics* **2003**, *22*, 2142−2150.

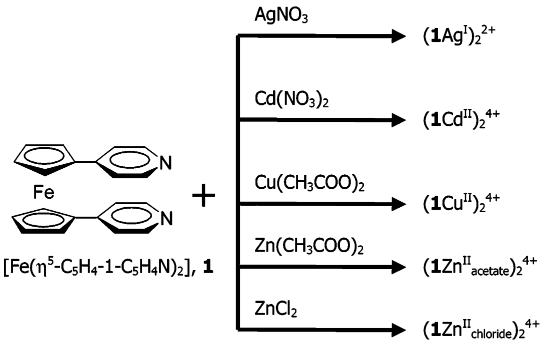
(7) (a) Liu, T.-Y.; Chen, Y. J.; Tai, C.-C.; Kwan, K. S. *Inorg. Chem.* **1999**, *38*, 674. (b) Hutchison, K.; Morris, J. C.; Nile, T. A.; Walsh; J. L.; Thompson, D. W.; Petersen, J. D.; Schoonover, J. R. *Inorg. Chem.* **1999**, *38*, 2516. (c) Barranco, E. M.; Crespo, O.; Gimeno, M. C.; Jones, P. G.; Laguna, A.; Villacampa, M. D. *J. Organomet. Chem.* **1999**, *592*, 258.

10.1021/om030432t CCC: \$25.00

Chart 1. Schematic Representation of the Relationship between Metallacycle and Network Formation



Scheme 1. Summary of the Reactions between 1 and Transition-Metal Salts



goal was that of exploiting, in parallel, the Lewis basicity of the N atoms to act as hydrogen bond acceptors in the formation of O−H- - -N (or $^-$O- - -H−N$^+$) bonds with suitable organometallic donor complexes, such as the ferrocenedicarboxylic acid complex $[Fe(\eta^5\text{-}C_5H_4COOH)_2]$.[9]

Ferrocene-based pyridyl ligands have been studied for the possibility of exploiting their redox properties in various applications, such as amperometric sensors for metal ions. The focus, however, has been mainly on monosubstituted ferrocenes,[10] while only few examples of bis-substituted ferrocene pyridyl complexes are known.[11] In particular, aminocobaltocenes and aminoferrocenes have been used to form complexes with Zn^{2+} and Co^{2+} metal ions.[11a]

A plethora of organic bidentate ligands are known and have been variously utilized in coordination. Of particular interest to our study is the flexible bis-*p*-aminopyridine bidentate ligand prepared by Hosseini et al. and utilized to prepare metallamacrocyclic complexes.[12] Our complex $[Fe(\eta^5\text{-}C_5H_4\text{-}4\text{-}C_5H_4N)_2]$ (**1**) can be seen as the organometallic analogue of the bis(pyridine) connector used by Hosseini. Indeed, the utilization of the preformed complex **1** as a ligand allows preparation of heterometallic metallamacrocycles with two metal centers.

In view of the conformational freedom of the two η^5-C_5H_4-1-C_5H_4N ligands in **1**, we were also intrigued by the question on whether the ligands would have adopted a cisoid or a transoid conformation upon coordination. While the former conformation leads to the formation of a finite coordination geometry, i.e. to a molecular complex (vide infra), the latter might, in principle, lead to an infinite network. The two limiting situations are shown in Chart 1.

In this paper we report the result of a systematic investigation of the reaction of **1** with a number of metal salts and complexes, e.g. $AgNO_3$, $Cu(CH_3COO)_2$, $Cd(NO_3)_2$, $ZnCl_2$, and $Zn(CH_3COO)_2$, which has yielded a whole family of novel heterobimetallic metallamacrocyclic derivatives, namely $[Fe(\eta^5\text{-}C_5H_4\text{-}1\text{-}C_5H_4N)_2]_2Ag_2(NO_3)_2\cdot 1.5H_2O$ ($(\mathbf{1}Ag^I)_2^{2+}$), $[Fe(\eta^5\text{-}C_5H_4\text{-}1\text{-}C_5H_4N)_2]_2Cd_2(NO_3)_4\cdot CH_3OH\cdot 0.5C_6H_6$ ($(\mathbf{1}Cd^{II})_2^{4+}$), $[Fe(\eta^5\text{-}C_5H_4\text{-}1\text{-}C_5H_4N)_2]_2Cu_2(CH_3COO)_4\cdot 3H_2O$ ($(\mathbf{1}Cu^{II})_2^{4+}$), $[Fe(\eta^5\text{-}C_5H_4\text{-}1\text{-}C_5H_4N)_2]_2Zn_2(CH_3COO)_4$ ($(\mathbf{1}Zn^{II}_{acetate})_2^{4+}$), and $[Fe(\eta^5\text{-}C_5H_4\text{-}1\text{-}C_5H_4N)_2]_2Zn_2Cl_4$ ($(\mathbf{1}Zn^{II}_{chloride})_2^{4+}$). The results of the reaction of the bidentate complex $[Fe(\eta^5\text{-}C_5H_4\text{-}1\text{-}C_5H_4N)_2]$ (**1**) with the salts $AgNO_3$, $Cu(CH_3COO)_2$, and $ZnCl_2$, respectively, have been reported in preliminary form.[13]

To compare the Lewis basicity of the pyridyl ligand in **1** toward metal coordination and toward a protic acid, we have also reacted **1** with the dicarboxylic organometallic acid $[Fe(\eta^5\text{-}C_5H_4COOH)_2]$, obtaining the hydrogen-bonded adduct $[Fe(\eta^5\text{-}C_5H_4\text{-}1\text{-}C_5H_4N)_2][Fe(\eta^5\text{-}C_5H_4COOH)_2]$ ($\mathbf{1}[Fe(\eta^5\text{-}C_5H_4COOH)_2]$).

Results and Discussion

The bidentate complex $[Fe(\eta^5\text{-}C_5H_4\text{-}1\text{-}C_5H_4N)_2]$ (**1**) was prepared as described in ref 6. Compound **1** is the precursor of all the molecular and supramolecular “complexes-of-complexes” described herein. The reactivity scheme is summarized in Scheme 1.

It is worth recalling that in the solid state complex **1** adopts an eclipsed conformation with the two pyridine moieties parallel and slightly tilted with respect to the cyclopentadienyl ligand planes.[6]

All compounds obtained according to Scheme 2 share a common feature, namely the formation of heterometallic metallamacrocycles. It will be seen that this is also the case of the hydrogen-bonded adduct $\mathbf{1}[Fe(\eta^5\text{-}C_5H_4COOH)_2]$, with the nonmarginal difference that the coordination to the heterometallic center is replaced by the direct complexation of two ferrocenyl moieties via a hydrogen bond. Furthermore, all heterometallic compounds show the presence of ancillary ligands bound to heterometallic centers. The separation between metal centers is also variable. Most relevant structural parameters are listed in Table 1.

Characterization of $(\mathbf{1}Ag^I)_2^{2+}$. The complex $(\mathbf{1}Ag^I)_2^{2+}$ has been obtained by reacting **1** with $AgNO_3$. The solid-state structure of the heterobimetallic system is shown in Figure 1. The eclipsed conformation observed in crystalline **1** is retained in crystalline $(\mathbf{1}Ag^I)_2^{2+}$. The two silver atoms interact directly with the pyridine ligands, with Ag- - -N distances of 2.125(8), 2.123(8) Å and 2.145-

---

[8] Constable, E. C.; Edwards, A. J.; Martinez-Mannez, R.; Raithby, P. R.; Thompson, C. Alexander, M. W. *J. Chem. Soc., Dalton Trans.* **1994**, 645.

[9] (a) Takusagawa, F.; Koetzle, T. F. *Acta Crystallogr., Sect. B* **1979**, *35*, 2888. (b) Palenik, G. J. *Inorg. Chem.* **1969**, *8*, 2744.

[10] *J. Organomet. Chem.* **2001**, 637−639 (whole issue).

[11] (a) Plenio, H.; Burth, D. *Organometallics* **1996**, *15*, 4054. (b) Constable, E. C.; Edwards, A. J.; Marcos, M. D.; Raithby, P. R.; Martinez-Manez, R.; Tendero, M. J. L. *Inorg. Chim. Acta* **1994**, *224*, 11. (c) Hall, C. D.; Truong, T. K. U.; Tucker, J. H. R.; Steed, J. W. *Chem. Commun.* **1997**, 2195.

[12] Schneider, R.; Hosseini, M. W.; Plainex, J. M.; De Cian, A.; Fisher, J. *Chem. Commun.* **1998**, 1625.

[13] Braga, D.; Polito, M.; Bracaccini, M.; D'Addario, D.; Tagliavini, E.; Proserpio, D. M.; Grepioni, F. *Chem. Commun.* **2002**, 1080.

Table 1. Relevant Structural Parameters (Distances in Å) in the Complexes $(\mathbf{1}Ag^{I})_2^{2+}$, $(\mathbf{1}Cd^{II})_2^{4+}$, $(\mathbf{1}Cu^{II})_2^{4+}$, $(\mathbf{1}Zn^{II}_{acetate})_2^{4+}$, $(\mathbf{1}Zn^{II}_{chloride})_2^{4+}$, and $\mathbf{1}[Fe(\eta^5\text{-}C_5H_4COOH)_2]$

distance	$(\mathbf{1}Ag^{I})_2^{2+}$	$(\mathbf{1}Cd^{II})_2^{4+}$	$(\mathbf{1}Cu^{II})_2^{4+}$	$(\mathbf{1}Zn^{II}_{acetate})_2^{4+}$	$(\mathbf{1}Zn^{II}_{clhoride})_2^{4+}$	$\mathbf{1}[Fe(\eta^5\text{-}C_5H_4COOH)_2]$
M- - -M[a]	3.500(2)	4.225(3)	3.428(5)	3.875(1)	6.125	
			3.473(5)			
M−N	2.125(8)	2.235(7)	2.03(3)	2.162(2)	2.034(8)	
	2.123(8)	2.244(6)	2.04(2)	2.192(3)	2.052(8)	
	2.145(8)	2.244(7)	2.01(3)			
	2.129(8)	2.254(7)	2.06(2)			
M−O[b]	2.752(9)	2.355(7)	1.96(2)	2.018(3)		
	2.870(1)	2.400(6)	2.49(2)	2.018(2)		
		2.450(6)	2.06(2)	2.042(3)		
		2.757(6)	2.37(2)			
M-Cl					2.202(3)	
					2.224(3)	
N- - -O_{COOH}						2.593(5)
						2.569(5)

[a] M = Ag, Cd, Cu, Zn. [b] O = $O_{nitrate}$, $O_{acetate}$.

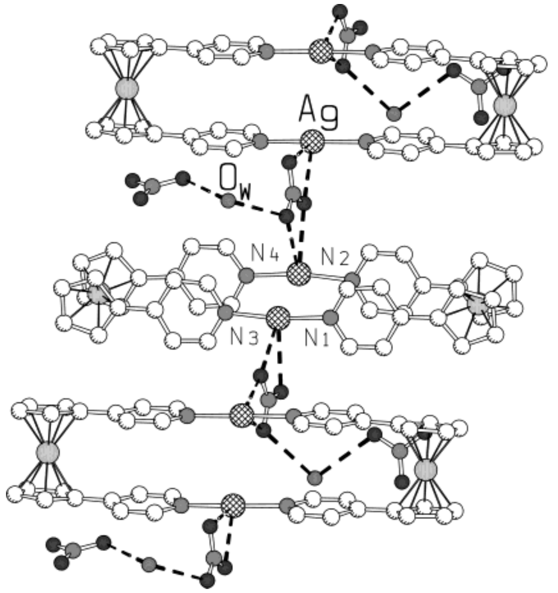


Figure 1. Interaction of the two Ag^+ cations for the complex $(\mathbf{1}Ag^{I})_2^{2+}$, with the pyridine ligands forming an Fe/Ag^{I} metallamacrocycle. One of the two nitrate anions is bound in a bridging mode to the Ag centers of adjacent metallacycles; the water molecules are hydrogen-bonded to both nitrate anions. Oxygen atoms of the nitrate anions and of the water molecules are shown as dark spheres.

(8), 2.129(8) Å for the two independent interactions, respectively.

The Ag- - -Ag distance is 3.500(2) Å. This separation is comparable to that observed in other dimeric Ag complexes.[14] The two nitrate anions play different roles in the crystal structure. While one is directly linked to the other nitrate anion via a water bridge, the second anion acts as a bridge between dimeric units, as shown in Figure 1, with O- - -Ag distances of 2.752(9) and 2.870(1) Å, respectively. A similar ion-pairing link between neighboring complexes has been observed in the complex with Ag^+ and bis(*p*-aminopyridine) bidentate ligands.[12] Analogously, neutral ligands (1,4-diazabicyclooctane, tetramethylpyrazine, and pyrazine) have been used to link silver carboxylates in extended networks.[15]

Characterization of $(\mathbf{1}Cd^{II})_2^{4+}$. The structure of $(\mathbf{1}Cd^{II})_2^{4+}$ is reminiscent of that of the silver complex. The formation of the metallacycle is observed in this compound and in the others described herein. However, although formation of the Ag−Ag system is not assisted by ancillary ligands, in the cadmium complex the two Cd centers are bridged by two asymmetric nitrate bridges (Cd(1)−O(9) = 2.355(7), Cd(2)−O(9) = 2.400(6), Cd(1)−O(1) = 2.450(6), Cd(2)−O(1) = 2.757(6) Å). While the coordination number around Cd(1) is 6, that around Cd(2) is 7, because of the additional presence of a coordinated methanol molecule (see Figure 2). In summary, one Cd atom is almost octahedral, while the other is heptacoordinated. The Cd- - -Cd distance is 4.225(3) Å.

The complexes of complexes form an elegant stepwise structure in the crystal (see Figure 2b). The ferrocenyl−pyridine systems stack at a distance of 3.47 Å, with the Cd atoms completely screened from the surroundings by the N and O interactions. The complex crystallizes as a benzene solvate (partial occupancy 50%). Figure 2c shows how the supramolecular arrangement of the complexes leaves ample channels throughout the structure where the solvent molecules can be accommodated.

Characterization of $(\mathbf{1}Cu^{II})_2^{4+}$. The complex $(\mathbf{1}Cu^{II})_2^{4+}$, obtained by reacting **1** with copper acetate, is shown in Figure 3. Similarly to $(\mathbf{1}Ag^{I})_2^{2+}$, the Cp−pyridine ligands are in an eclipsed conformation and bridge the two Cu atoms. The Cu- - -Cu separations are 3.428(5) and 3.473(5) Å, respectively, for the two independent half-molecules in the asymmetric unit. Similarly to what is observed in $(\mathbf{1}Cd^{II})_2^{4+}$, the bimetallic Cu- - -Cu unit is spanned by two acetate anions (Cu(1)−O(2) = 1.96(2), 2.49(2) Å, Cu(2)−O(6) = 2.06(2), 2.37(2) Å). If one considers the additional acetate ions linked to each Cu atom, the coordination around copper can be described as distorted square pyramidal. The outer O atoms of the dangling acetate units are involved in OH_{water}- - -$O_{acetate}$ interactions with the water molecules (O(1)- - -O(9) = 2.75(4), O(5)- - -O(11) = 2.81(3), O(7)- - -O(11) = 2.70(4) Å) and/or in short C−H- - -$O_{acetate}$ interactions, with the CH groups belonging to the six-membered rings of the Cp−pyridine ligands (five C(H)- - -$O_{acetate}$ interactions in the range 3.33(3)−3.47(3) Å). The supramolecular organization of the complexes is shown in Figure 3.

Characterization of $(\mathbf{1}Zn^{II}_{acetate})_2^{4+}$. The complex obtained by reacting **1** with zinc acetate, $(\mathbf{1}Zn^{II}_{acetate})_2^{4+}$,

---

(14) (a) Su, C. Y.; Kang, B. S.; Wang, Q. G. *J. Chem. Soc., Dalton Trans.* **2000**, 1831. (b) Eastland, G. W.; Mazid, M. A.; Russell, D. R.; Symons, M. C. R. *J. Chem. Soc., Dalton Trans.* **1980**, 1682.

(15) Brammer, L.; Burgard, M. D.; Rodger, C. S.; Swearingen, J. K.; Rath, N. P. *Chem. Commun.* **2001**, 2468.

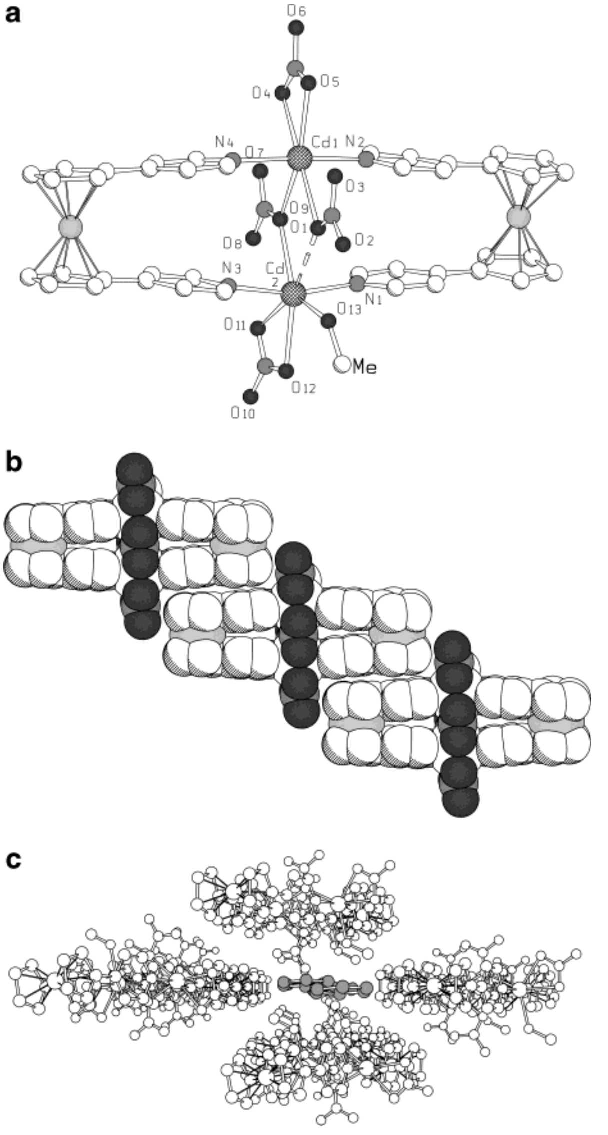


Figure 2. (a) Asymmetric bridging of the two Cd centers in $(\mathbf{1}Cd^{II})_2{}^{4+}$ by two nitrate anions. Note how Cd(2) also interacts with a methanol molecule. Both Cd atoms carry also a chelating nitrate anion. (b) Complexes of complexes forming an elegant stepwise structure in the crystal, with π-stacking between ferrocenyl and pyridine moieties. (c) Supramolecular arrangement of the complexes, leaving ample channels throughout the structure where the benzene solvent molecules can be accommodated.

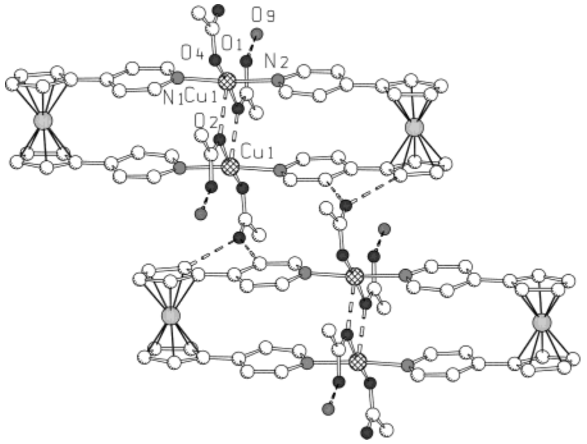


Figure 3. The Fe/Cu^{II} metallamacrocycle of **1** with copper, $(\mathbf{1}Cu^{II})_2{}^{4+}$. O atoms are represented as dark spheres and H atoms are omitted for clarity. The supramolecular organization of the complexes shows the interactions of the $O_{acetate}$- - -O_{water} and C−H- - -O types (broken lines) between pyridyl and cyclopentadienyl CH groups and the acetate oxygens. Only one of the two independent molecules is shown.

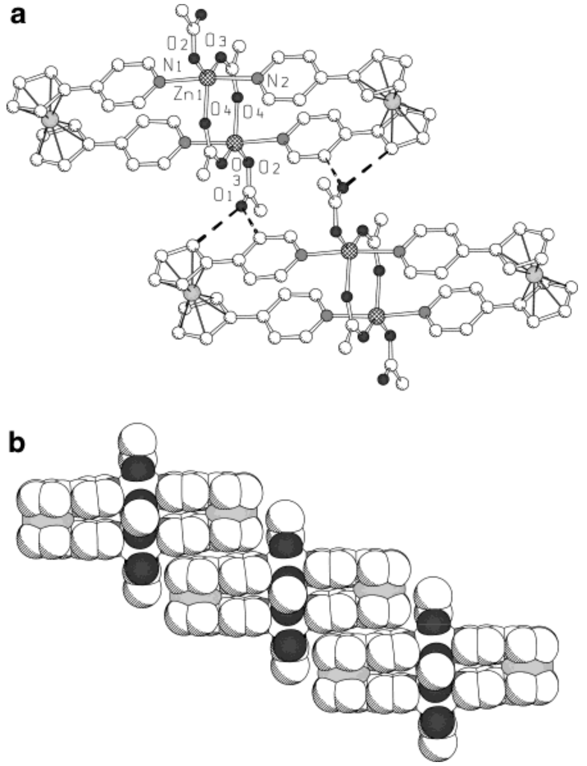


Figure 4. (a) Similarity of the rectangular structure of $(\mathbf{1}Zn^{II}{}_{acetate})_2{}^{4+}$ to that of $(\mathbf{1}Cu^{II})_2{}^{4+}$, with the acetate anions bound in bridging and terminal fashions (compare with Figure 3). O atoms are represented as dark spheres. H atoms are omitted for clarity. (b) Space-filling representation of the packing of $(\mathbf{1}Zn^{II}{}_{acetate})_2{}^{4+}$ in the solid state. Note how the outer structure is very similar also to that of $(\mathbf{1}Cd^{II})_2{}^{4+}$ (see Figure 2b) and forms, analogously, a stepladder arrangement with π-stacking between ferrocenyl and pyridine moieties.

possesses a structure very similar to that of $(\mathbf{1}Cu^{II})_2{}^{4+}$. The Cp−pyridine ligands are nearly eclipsed, with a Zn- - -Zn separation of 3.875(1) Å. As in $(\mathbf{1}Cu^{II})_2{}^{4+}$, two acetate ligands span the Zn- - -Zn system (Zn(1)- - -O(3) = 2.018(3), Zn(1)−O(4) = 2.018(2) Å), while two acetate ligands are dangling externally at a Zn- - -O separation of 2.042(3) Å (see Figure 4). The Zn- - -Zn distance indicates that the interaction between the Zn centers is entirely repulsive, as would be expected from closed-shell first-row systems. The coordination around the Zn centers can be described as a trigonal bipyramid. A space-filling representation of the packing of $(\mathbf{1}Zn^{II}{}_{acetate})_2{}^{4+}$ in the solid state is shown in Figure 4b. It is noteworthy how the outer structure of $(\mathbf{1}Zn^{II}{}_{acetate})_2{}^{4+}$ is also very similar to that of $(\mathbf{1}Cd^{II})_2{}^{4+}$ and, analogously, forms a stepladder arrangement with π-stacking between ferrocenyl and pyridine moieties (average π-stack distance 3.48 Å). As in the previous cases, the “free” acetate O atoms take part in C−H- - -O interactions with the ferrocenyl and pyridine units.

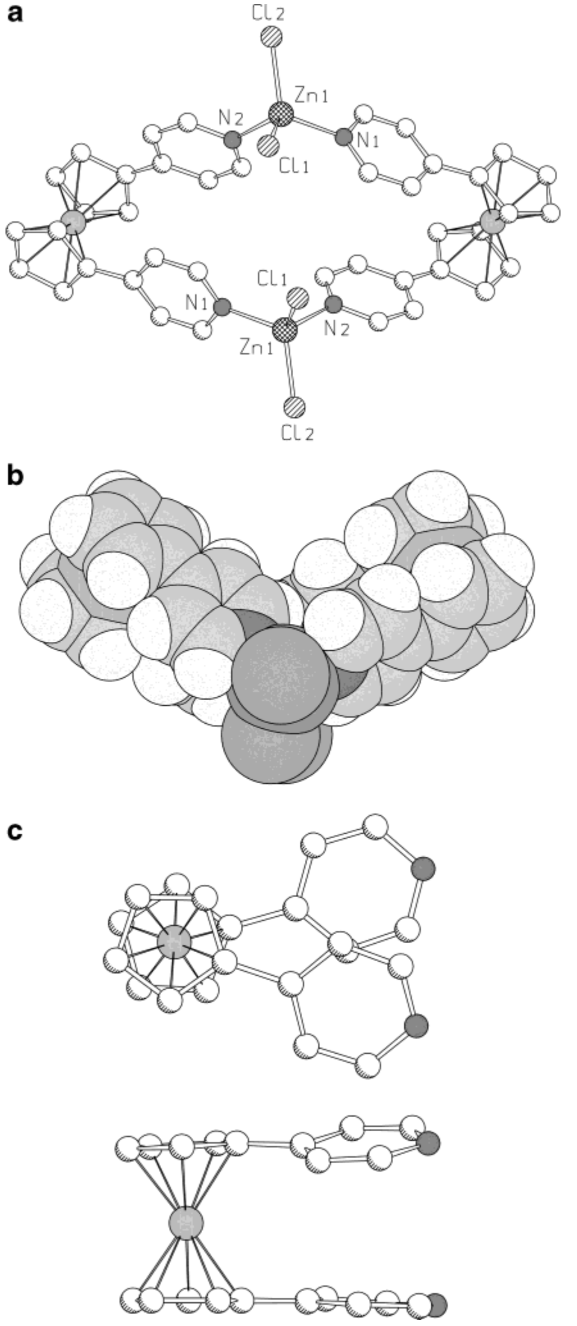


Figure 5. (a) Fe/Zn^{II} metallamacrocycle of **1** with zinc chloride, ($\mathbf{1}$Zn$^{II}{}_{chloride}$)$_2{}^{4+}$. (b) Side view (space filling) showing the butterfly shape of the complex. (c) (top) Staggered conformation of the cyclopentadienyl rings (top) and tilting of the pyridine ring planes in the organometallic ligand (bottom).

Characterization of ($\mathbf{1Zn^{II}{}_{chloride}}$)$_\mathbf{2}{}^{\mathbf{4+}}$. The complex obtained by reacting **1** with zinc chloride, ($\mathbf{1}$Zn$^{II}{}_{chloride}$)$_2{}^{4+}$, is shown in Figure 5a. In contrast to all the other complexes described above, including the Zn complex ($\mathbf{1}$Zn$^{II}{}_{acetate}$)$_2{}^{4+}$, the constraint imposed by the tetrahedral coordination around the zinc centers (Zn−Cl distances 2.202(3), 2.224(3) Å) leads to the formation of a butterfly-type molecule, with the two ZnCl$_2$ units forming the hinge and the ferrocenyl units the wings of the butterfly (see Figure 5b for a space-filling representation). The distance between the two Zn centers is, in this molecule, 6.125 Å. The tetrahedral coordination also forces the cyclopentadienyl rings into a staggered conformation, as shown in Figure 5c (top); at the same time the pyridine ring planes, which are parallel in the ($\mathbf{1}$Zn$^{II}{}_{acetate}$)$_2{}^{4+}$ complex, are tilted by ca. 16° with respect to each other (see Figure 5c, bottom).

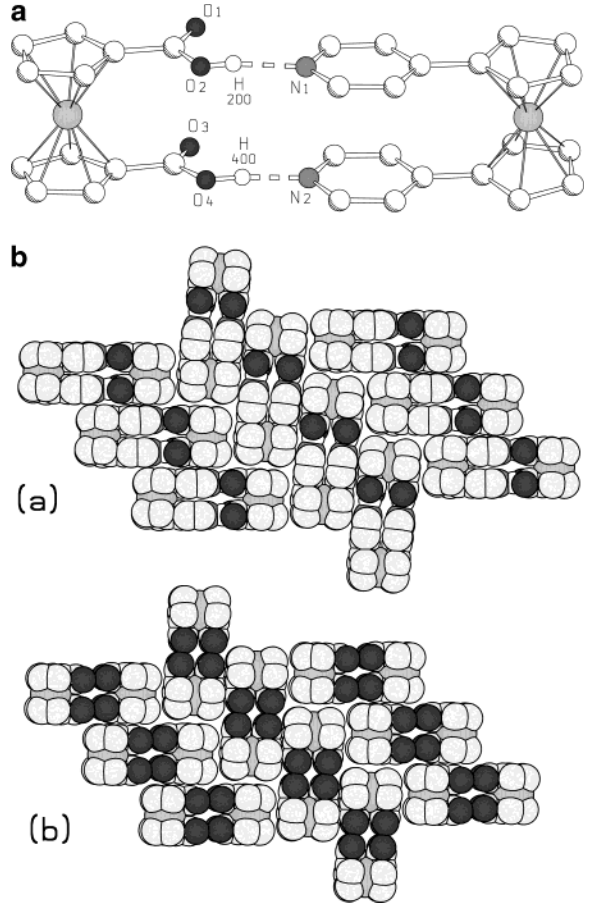


Figure 6. (a) View of the supramolecular adduct **1**[Fe(η^5-C$_5$H$_4$COO)$_2$], showing the hydrogen bonds between the O−H donors on **1** and the N acceptors on the [Fe(η^5-C$_5$H$_4$-1-C$_5$H$_4$N)$_2$] moiety. (b) Comparison of the packing arrangements in **1**[Fe(η^5-C$_5$H$_4$COOH)$_2$] (top) and the monoclinic form of the complex [Fe(η^5-C$_5$H$_4$COOH)$_2$] (bottom).

Characterization of the Hydrogen Bond Adduct (1[Fe($\boldsymbol{\eta^5}$-C$_\mathbf{5}$H$_\mathbf{4}$COOH)$_\mathbf{2}$]). Although chemically different, the reaction of **1** with the ferrocenedicarboxylic acid [Fe(η^5-C$_5$H$_4$COOH)$_2$] bears an interesting relationship with the complexes of complexes described above. The supramolecular structure of the hydrogen bond adduct [Fe(η^5-C$_5$H$_4$-1-C$_5$H$_4$N)$_2$][Fe(η^5-C$_5$H$_4$COOH)$_2$] is shown in Figure 6a. It can be seen that **1** establishes with [Fe(η^5-C$_5$H$_4$COOH)$_2$] a twin hydrogen bonding interaction, forming a sort of ferrocenyl dimer. The O- - -N separations (O(2)- - -N(1) = 2.593(5), O(4)- - -N(2) = 2.569(5) Å) are in agreement with the presence of conventional hydrogen bonds. It is interesting to observed that, judging from the diffraction data, no proton transfer from the −COOH groups to the N sites takes place. Hence, the two hydrogen bonding interactions ought to be described as neutral O−H- - -N rather than as “charge assisted” $^-$O- - -H−N$^+$ hydrogen bonds.[16] Both the two COOH groups in the diacid and the pyridine groups in **1** are eclipsed. The arrangement is thus topologically related to that observed in all complexes discussed above with the exception of ($\mathbf{1}Zn^{II}_{chloride})_2^{4+}$. It is interesting to note that the preference for an eclipsed conformation of the pyridyl ligands is maintained in the formation of the hydrogen bond adduct.

In principle, $\mathbf{1}[Fe(\eta^5\text{-}C_5H_4COOH)_2]$ could possess an alternative network structure in the solid state based on 1-D chains of alternating pyridyl−carboxylic ligands. This arrangement is fairly common when ferrocenedicarboxylic acid is used. It has been observed in hydrogen-bonded adducts with bis-amidines[17] and with other bis-amines, such as 1,4-diazabicyclo[2.2.2]octane ($C_6H_{12}N_2$, DABCO).[18] In all these cases, however, the geometry of the base did not allow cyclization and *forced* the system to chain formation.

A similar situation is seen also when one looks at the diacid $[Fe(\eta^5\text{-}C_5H_4COOH)_2]$ itself.[9] In contrast to most dicarboxylic acids that form chains linked by carboxylic rings, the ferrocenyl diacid forms cyclic dimers joined by a twin carboxylic ring in both of its known polymorphic modifications (monoclinic and triclinic). It is noteworthy that the analogy between $\mathbf{1}[Fe(\eta^5\text{-}C_5H_4COOH)_2]$ and $[Fe(\eta^5\text{-}C_5H_4COOH)_2]$ is not confined to the dimeric structure: the supramolecular arrangement in the solid state is also extremely similar. Figure 6b shows a comparison of the packing arrangements in the crystal of $\mathbf{1}[Fe(\eta^5\text{-}C_5H_4COOH)_2]$ and in that of the monoclinic form of the diacid.

Conclusions

In this paper we have shown that preformed organometallic molecules such as **1** with intermolecular bonding capacity can be used to prepare novel mixed-metal macrocyclic complexes.

It is worth noting that ligand **1** seems uniquely set up ("partially preorganized") for forming these kinds of discrete complexes. In solution, depending on the concentration, it is likely that discrete 2:2 complexes are the major species and hence crystallize as metallacycles.

It is interesting to compare the structure of the complex $(\mathbf{1}Ag^I)_2^{2+}$ with that obtained by using 1,1′-bis-(2-pyridyl)ferrocene.[19a] The location of the N atom does not allow dimerization but chelation at the Ag atoms. The complex is, however, aggregated in a dimeric unit via perchlorate bridges. In a related example, the 1,1′-bis-(2-pyridyl)octamethylferrocene is linked to two $PtCl_2(C_2H_4)$ units in a divergent fashion, whereas with Cu^I the ligand acts, as in the Ag case, as a chelating ligand.[19b] The utilization of dimetallic units has been demonstrated to be a viable route to obtain a variety of supramolecular and crystal architectures.[20]

The presence of network/molecule isomers, whereby the ferrocenyl ligand can take advantage of the conformation freedom around the metal center to form extended networks rather than finite complexes, is being investigated.

Experimental Section

General Information. All the experimental manipulations involving the synthesis of $[Fe(\eta^5\text{-}C_5H_4\text{-}1\text{-}C_5H_4N)_2]$ were carried out under dry argon. Anhydrous solvents (DME, methylcyclohexane, ether) were purchased from Aldrich in SureSeal bottles. All other chemicals were obtained from Aldrich and used as received. The compound $[Fe(\eta^5\text{-}C_5H_4C_6H_4N)_2]$ (**1**) has been prepared as previously reported.[6]

Synthesis of $[Fe(\eta^5\text{-}C_5H_4\text{-}1\text{-}C_5H_4N)_2]_2Ag_2(NO_3)_2\cdot 1.5H_2O$. Crystals of $(\mathbf{1}Ag^I)_2^{2+}$ were obtained by layering a MeOH solution of the $Ag(NO_3)$ (0.006 g, 0.035 mmol, in 5 mL) onto a benzene solution of the ligand 1,1′-bis(4-pyridyl)ferrocene (**1**; 0.030 g, 0.088 mmol, in 15 mL). After 2 days the solution was filtered and single crystals were isolated as red prisms. Yield: 63% for $(\mathbf{1}Ag^I)_2^{2+}$. Anal. Calcd for $(\mathbf{1}Ag^I)_2^{2+}$: C, 48.47; H, 3.56; N, 8.48. Found: C, 48.34; H, 3.40; N, 8.33.

Synthesis of $[Fe(\eta^5\text{-}C_5H_4\text{-}1\text{-}C_5H_4N)_2]_2Cd_2(NO_3)_4\cdot CH_3OH\cdot 0.5C_6H_6$. Red single crystals of $(\mathbf{1}Cd^{II})_2^{4+}$ were obtained by layering a solution of $Cd(NO_3)_2\cdot 4H_2O$ in methanol over a benzene solution of the ligand **1** (0.031 g, 0.091 mmol). Yield: 73% for $(\mathbf{1}Cd^{II})_2^{4+}$. Anal. Calcd for $(\mathbf{1}Cd^{II})_2^{4+}$: C, 44.68; H, 3.35; N, 8.87. Found: C, 44.56; H, 3.30; N, 8.81.

Synthesis of $[Fe(\eta^5\text{-}C_5H_4\text{-}1\text{-}C_5H_4N)_2]_2Cu_2(CH_3COO)_4\cdot 3H_2O$. Red prismatic crystals of $(\mathbf{1}Cu^{II})_2^{4+}$ were obtained by layering an MeOH solution of $Cu(CH_3COO)_2\cdot 2H_2O$ (0.007 g, 0.032 mmol) over a benzene solution of the ligand **1** (0.037 g, 0.109 mmol in 15 mL). Yield: 68% for $(\mathbf{1}Cu^{II})_2^{4+}$. Anal. Calcd for $(\mathbf{1}Cu^{II})_2^{4+}$: C, 52.52; H, 4.59; N, 5.10. Found: C, 52.40; H, 4.42; N, 5.08.

Synthesis of $[Fe(\eta^5\text{-}C_5H_4\text{-}1\text{-}C_5H_4N)_2]_2Zn_2(CH_3COO)_4$. $(\mathbf{1}Zn^{II}_{acetate})_2^{4+}$ was prepared by refluxing for 1 h a solution obtained by dissolving **1** (0.028 g, 0.082 mmol) and $Zn(CH_3COO)_2$ (0.015 g, 0.082 mmol) in 5 mL of methanol. Red crystals suitable for X-ray diffraction were obtained by slow cooling of the methanol solution. Yield: 80% for $(\mathbf{1}Zn^{II}_{acetate})_2^{4+}$. Anal. Calcd for $(\mathbf{1}Zn^{II}_{acetate})_2^{4+}$: C, 55.04; H, 4.23; N, 5.35. Found: C, 54.95; H, 4.17; N, 5.29.

Synthesis of $[Fe(\eta^5\text{-}C_5H_4\text{-}1\text{-}C_5H_4N)_2]_2Zn_2Cl_4$. Red crystalline prisms of $(\mathbf{1}Zn^{II}_{chloride})_2^{4+}$ were obtained by layering a MeOH solution of $ZnCl_2$ (0.007 g, 0.051 mmol) over a benzene solution of the ligand **1** (0.037 g, 0.109 mmol in 15 mL). Yield: 70% for $(\mathbf{1}Zn^{II}_{chloride})_2^{4+}$. Anal. Calcd for $(\mathbf{1}Zn^{II}_{chloride})_2^{4+}$: C, 54.46; H 3.66; N, 6.35. Found: C, 54.38; H, 3.54; N, 6.29.

Synthesis of $[Fe(\eta^5\text{-}C_5H_4\text{-}1\text{-}C_5H_4N)_2][Fe(\eta^5\text{-}C_5H_4COOH)_2]$. Crystals of $\mathbf{1}[Fe(\eta^5\text{-}C_5H_4COOH)_2]$ were obtained by slow evaporation at room temperature of a solution prepared by dissolving **1** (0.015 g, 0.044 mmol) and $[Fe(\eta^5\text{-}C_5H_4COOH)_2]$ (0.012 g, 0.044 mmol) in 4 mL of methanol. Anal. Calcd for $\mathbf{1}[Fe(\eta^5\text{-}C_5H_4COOH)_2]$: C, 62.57; H, 4.27; N, 4.56. Found: C, 62.38; H, 4.25; N, 4.55.

Crystallography. Crystal data and details of measurements for the compounds $(\mathbf{1}Cd^{II})_2^{4+}$, $(\mathbf{1}Zn^{II}_{acetate})_2^{4+}$, and $\mathbf{1}[Fe(\eta^5\text{-}C_5H_4COOH)_2]$ are reported in Table 2. The structures of $(\mathbf{1}Zn^{II}_{clhoride})_2^{4+}$, $(\mathbf{1}Cu^{II})_2^{4+}$, and $(\mathbf{1}Ag^I)_2^{2+}$ have been reported in a preliminary communication[13] (CCDC 177935-177937).

For the compounds $(\mathbf{1}Cd^{II})_2^{4+}$ (223 K) and $\mathbf{1}[Fe(\eta^5\text{-}C_5H_4COOH)_2]$ X-ray data were collected on a Nonius CAD-4 diffractometer. For the compound $(\mathbf{1}Zn^{II}_{acetate})_2^{4+}$ X-ray diffrac-

---

(16) Proton transfer and competition between O−H···N and $^-$O···H−N$^+$ interactions are dealt with in, for instance: (a) Wilson, C. C. *Acta Crystallogr., Sect. B* **2001**, *57*, 435. (b) Steiner, T.; Majerz, I.; Wilson, C. *Angew. Chem., Int. Ed.* **2001**, *40*, 2651. (c) Wiechert, D.; Mootz, D. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 1974. (d) Braga, D.; Maini, L.; de Sanctis, G.; Rubini, K.; Grepioni, F.; Chierotti, M. R.; Gobetto, R. *Chem. Eur. J.*, in press. (e) Braga, D.; Maini, L.; Polito, M.; Grepioni, F. *Struct. Bonding*, in press.

(17) Braga, D.; Maini, L.; Grepioni, F.; DeCian, A.; Felix, O.; Fisher, J.; Hosseini, M. W. *New J. Chem.* **2000**, *24*, 547.

(18) (a) Braga, D.; Maini, L.; Polito, M.; Mirolo, L.; Grepioni, F. *Chem. Commun*. **2002**, 2960. (b) Zakaria, C. M.; Ferguson, G.; Lough, A. J.; Glidewell, C. *Acta Crystallogr., Sect B* **2002**, *58*, 786.

(19) (a) Tani, K.; Mihana, T.; Yamagata T.; Saito, T. *Chem. Lett.* **1991**, 2047. (b) Neumann, B.; Siemeling, U.; Stammler, H. G.; Vorfeld, U.; Delis, J. G. P.; Leeuwen, P. W. N. M.; Vrieze, K.; Fraanje, J.; Goubitz, K.; Fabrizi de Biani, F.; Zanello, P. *J. Chem. Soc., Dalton Trans.* **1997**, 4705.

(20) (a) Cotton, F. A.; Lin, C.; Murillo, C. A. *Acc. Chem. Res.* **2001**, *34*, 759. (b) Rosi, N. L.; Eddaoudi, M.; Kim, J.; O'Keeffe, M.; Yaghi, O. M. *CrystEngComm* **2002**, *4*, 401.

Table 2. Crystal Data and Details of Measurements for the Compounds $(1\mathrm{Cd^{II}})_2^{4+}$, $(1\mathrm{Zn^{II}}_{\mathrm{acetate}})_2^{4+}$ and $1[\mathrm{Fe}(\eta^5\text{-}\mathrm{C_5H_4COOH})_2]$

	$(\mathbf{1}\mathrm{Cd^{II}})_2^{4+}$	$(\mathbf{1}\mathrm{Zn^{II}}_{\mathrm{acetate}})_2^{4+}$	$\mathbf{1}[\mathrm{Fe}(\eta^5\text{-}\mathrm{C_5H_4COOH})_2]$
formula	$C_{44}H_{38}Cd_2Fe_2N_8O_{13}$	$C_{48}H_{44}Fe_2N_4O_8Zn_2$	$C_{32}H_{26}Fe_2N_2O_4$
M_w	1223.32	1047.31	614.25
cryst syst	triclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a (Å)	11.866(7)	8.3153(2)	14.404(2)
b (Å)	13.968(3)	9.6967(3)	9.018(3)
c (Å)	16.064(3)	13.8748(4)	19.324(2)
α (deg)	110.21(2)	76.304(2)	90
β (deg)	105.16(3)	86.908(1)	96.10(2)
γ (deg)	93.11(3)	73.066(1)	90
V (Å^3)	2381(2)	1039.66(5)	2495.9(9)
Z	2	1	4
T (K)	233	153	293
F(000)	1220	536	1264
μ(Mo Kα) (mm^{-1})	1.550	1.887	1.207
no. of measd rflns	6868	7698	7439
no. of unique rflns	6591	4508	7247
no. of params	571	274	331
GOF on F^2	0.993	0.923	0.943
R1 (on F ($I > 2\sigma(I)$))	0.0564	0.0443	0.0430
wR2 (on F^2, all data)	0.1711	0.1158	0.1347

tion data were collected on a Nonius Kappa CCD instrument. Common to all compounds was a graphite monochromator (Mo Kα radiation, $\lambda = 0.710\ 73$ Å) and ψ-scan absorption correction. All non-H atoms in the remaining compounds (except for the C_{benzene} atoms in $(\mathbf{1}\mathrm{Cd^{II}})_2^{4+}$) were refined anisotropically. H atoms bound to C atoms were added in calculated positions. H atoms of the $-$COOH groups in $\mathbf{1}[\mathrm{Fe}(\eta^5\text{-}\mathrm{C_5H_4COOH})_2]$ were found to be bound to the oxygen atoms. The computer program SHELXL97[21a] was used for structure solution and refinement. The computer program SCHAKAL99[21b] was used for all graphical representations. For the evaluation of hydrogen bonding parameters the program PLATON was used.[21c]

Acknowledgment. We thank MIUR (COFIN and FIRB) and the Universities of Bologna (D.B., E.T.). Milano (D.M.P.) and Sassari (F.G.) for financial support. M.P. thanks the program Marco Polo (University of Bologna) for financing a research stage at King's College London.

Supporting Information Available: Details about the X-ray crystal structures, including tables of crystal data and structure refinement, atomic coordinates, bond lengths and angles, and anisotropic displacement parameters and ORTEP figures for the compounds $(\mathbf{1}\mathrm{Cd^{II}})_2^{4+}$, $(\mathbf{1}\mathrm{Zn^{II}}_{\mathrm{acetate}})_2^{4+}$, and $\mathbf{1}[\mathrm{Fe}(\eta^5\text{-}\mathrm{C_5H_4COOH})_2]$. This material is available free of charge via the Internet at http://pubs.acs.org.

OM030432T

---

[21] (a) Sheldrick, G. M. SHELX97, Program for Crystal Structure Determination; University of Göttingen: Göttingen, Germany, 1997. (b) Keller, E. SCHAKAL99, Graphical Representation of Molecular Models; University of Freiburg, Freiburg, Germany, 1999. (c) Spek, A. L. *Acta Crystallogr., Sect. A* **1990**, *46*, C31.