A Calix[4]arene-Based Bipyridine Podand as Versatile Ligand for Transition Metal Cations

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The calix[4]arene-based podand **1** which incorporates two 2,2′-bipyridine units and two benzyl units in alternate positions at the lower rim has been subjected to complexation studies with copper(I), copper(II), cobalt(II), nickel(II), and zinc(II). The reaction of **1** with $Cu(MeCN)_4PF_6$ afforded the expected mononuclear Cu^I complex. With cobalt(II), nickel(II), and zinc(II) chloride, **1** gave dinuclear tetrahedral complexes in which each bipyridine unit is associated to two chlorine atoms around the metal centre. With Zn^{II}, replacing the chloride ion for the trifluoromethanesulfonate ion resulted in the formation of the mononuclear complex species. The complexes thus obtained were fully characterised, notably by NMR techniques and, for the dinuclear cobalt, nickel and zinc species, by X-ray crystal structure analyses.
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1. Introduction

The abundant literature related to calixarenes illustrates their important role in supramolecular chemistry,[1] and particularly, as recently reviewed by Asfari et al.[2] or by Matt et al. or Roundhill et al.,[3] as ligands for metal cations. Their complexation properties are attractive in the development of selective extracting agents for metallic cations, notably for rare metals. This can be accomplished through their own binding sites (oxygen atoms, aryl rings), or by their ability to act as carriers and spatial organisers of various types of chelating agents, such as ethers, esters, amides and their thio analogues, ketones, alkenes, ammonium species, amino acids, phosphanes, or heterocycles.

Among these chelating subunits, introduced at the upper or lower rims at the calix[4]arene platform, the biheterocyclic systems have been moderately studied, with a major attention brought to the 2,2′-bipyridine group,[4] and to the corresponding Ru^{II}, Cu^I, and Ag^I complexes. Other contributions have been devoted to ligands incorporating 2,2′-bithiazole[5] or 2,2′-bipyrazine,[6] and their Cu^I complexes.

Depending on the nature, the number and the position of the chelating units, such podands should be able to provide different coordination geometries. We thus attempted to employ this behaviour in a selective metal extraction process based on the use of the tetrahedral geometry. In this sense, we have recently demonstrated the interest of such kinds of complexing structures with the bis(bipyridyl) ligand **1** displaying in alternate positions two opposing 2,2′-bipyridyl chelating subunits and two opposing lipophilic pendant benzyl groups. Complex **1** showed a very interesting selective and quantitative extraction behaviour towards Ag^I against Pb^{II} from neutral aqueous media.[7]

The objective of the present report was to verify the complexing behaviour of **1** toward various transition metal cations. We found this necessary because, on the one hand, except for the above-mentioned metallic cations, the coordinating behaviour of such ligands towards transition metal species has not been reported until now, and on the other hand our extraction study necessitated a better knowledge of the other available complexes.

As assessed by X-ray crystallographic study of its picolyl parent compound **A**,[8] complex **1** should give a mononuclear Cu^I pro-helicoidal tetrahedral complex, which should also be encountered with Ag^I in complex **B**.[7,9] With $CoCl_2$, we recently reported the synthesis and X-ray crystal structure determination of a mononuclear complex involving a calix[4]arene podand at the upper rim by a 2,2′-bipyridyl unit, and in which the metal centre was coordinated in a tetrahedral mode by the two chloride ions and the two bipyridyl nitrogen atoms.[4f] This structure was proposed some years ago by Newkome et al. for 6,6′-dimethyl-2,2′-bipyridine and $CoCl_2$, $NiCl_2$, $ZnCl_2$, $CuCl_2$, as well as less common metal species.[10] With the two close bipyridyl units of

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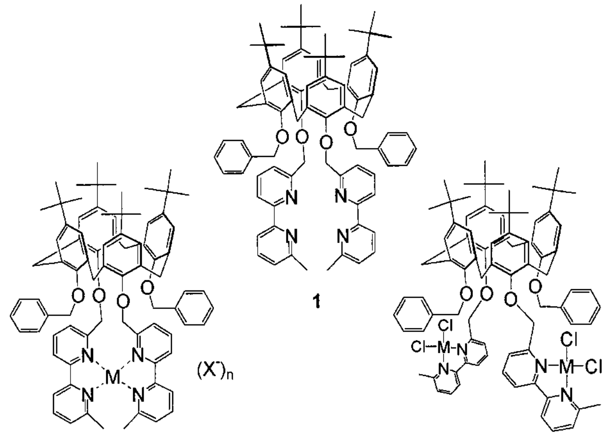
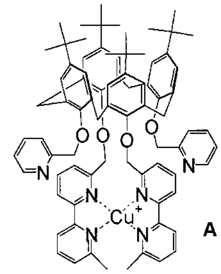


M = Cu(I), n = 1, X⁻ = PF₆ : **2**
M = Zn(II), n = 2, X⁻ = CF₃SO₃ : **6**
M = Ag(I), n = 1, X⁻ = PF₆ : **B**

M = Co(II) : **3**
Ni(II) : **4**
Zn(II) : **5**



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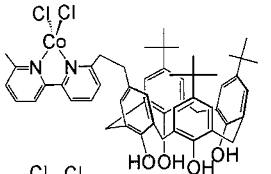

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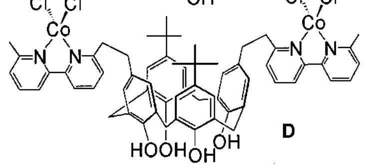

D

1, one may expect the two coordinating chlorine atoms to be replaced by the second bipyridine unit, thus affording mononuclear complexes with Co^{II}, Ni^{II}, Zn^{II}, and Cu^{II}; however, dinuclear complexes could be obtained.

2. Synthesis and Analysis of Complexes

The bis(benzyl) bis(bipyridyl) podand **1** was prepared as previously reported.[7] The air-stable orange copper(I) complex, **2**, was synthesised by mixing stoichiometric amounts of ligand **1** and $Cu(CH_3CN)_4PF_6$ in CH_3CN. It was obtained in a pure state with a yield of 90% after chromatography on alumina with CH_2Cl_2 as eluent. The ML stoichiometry was preliminarily determined by UV titration, with the appearance of the characteristic MLCT (Metal-to-Ligand Charge Transfer) band at 447 nm; the ε value of 5500 $dm^3 \cdot mol^{-1} \cdot cm^{-1}$, measured with a CH_2Cl_2 solution of **2**, is similar to those of the parent complexes.[4b,4e] Electrospray mass spectrometry (positive mode, 60 V) showed the presence of the monocharged 1:1 adduct [**1** + Cu]$^+$, characterised by a base peak at 1257.7 amu, and elemental analysis was consistent with the proposed formula. ^{1}H NMR study of **2** (Figure 1) showed strong similitude with parent species,[4e] and with its picolyl analogue **A**,[8] for which the racemic pro-helicoidal metal-centred structure was demonstrated by X-ray analysis. More particularly, the helicoidal arrangement of the two bipyridine units was evident by the presence of an AB system at $\delta = 5.00, 6.35$, attributed to the two corresponding anchoring methylene groups. In the grooves thus generated, the benzyl groups should have place, resulting in the discrimination of the two enantiotopic OCH_2 protons, characterised by a strong AB system at $\delta = 3.82, 4.01$.

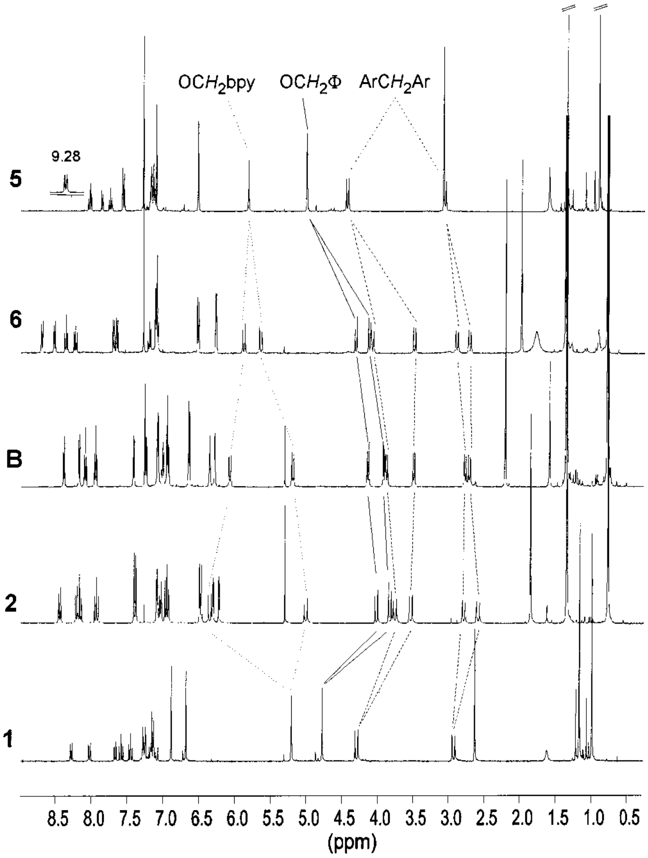

Figure 1. ^{1}H NMR spectra of **1**, **2**, **B**, **6** and **5** (500 MHz, $CDCl_3$, room temp.)

As previously experienced at the upper rim of the calix[4]arene (complexes **C** and **D**) and assessed by a crystal structure (complex **C**),[4f] the cobalt(II) chloride can be complexed by a bipyridine unit in a tetrahedral mode involving two chloride ions and the two bipyridyl nitrogen atoms.[10]

The blue-green complex **3** was prepared by adding an excess of $CoCl_2$ to **1** in a mixture of CH_3CN and CH_2Cl_2 at room temperature; due to its good solubility in CH_2Cl_2, **3** was easily separated from excess $CoCl_2$ in a highly pure form. The dinuclear nature of **3** was indicated by UV/Vis spectroscopy, which showed the presence of the expected metal-centred transition at 658 cm^{-1}, with a molar extinction coefficient of ca. 1000 $dm^3 \cdot mol^{-1} \cdot cm^{-1}$, twice the value reported for complex **C**, and identical to that of complex **D**. Elemental analysis was consistent with the formula $C_{82}H_{88}Co_2Cl_4N_4O_4$. Electrospray mass spectrometry (positive mode, 252 V) showed notably the presence of the expected mono-charged species [**1** + 2 $CoCl_2$ − Cl]$^+$ at 1417.5 amu (10%), accompanied by the "decomplexed" species, such as [**1** + $CoCl_2$ − Cl]$^+$ at 1287.5 amu (40%), [**1** + Na]$^+$

at 1216.7 amu (100%), [**1** + H]$^+$ at 1193.7 amu (60%), and by various fragmentation products.

In the standard ^{1}H NMR spectrum of **3** ($\delta = 0-15$), the absence of some resonance signals confirmed the paramagnetic nature of the [Co/bpy] subunit, as was previously observed.[4f] Recording data in a larger frequency domain (65000 Hz; $\delta = 216$ at 300 MHz, $\delta = 130$ at 500 MHz) showed 11 new resonance signals that were correlated by a COSY experiment (Figure 2): two groups of three singlets integrating 2 H each at $\delta = 72.93$ ($\Delta\nu_{1/2} = 32$ Hz), 42.28 ($\Delta\nu_{1/2} = 34$ Hz), -6.75 (s, $\Delta\nu_{1/2} = 77$ Hz), and $\delta = 72.72$ (s, $\Delta\nu_{1/2} = 25$ Hz), 49.18 (s, $\Delta\nu_{1/2} = 28$ Hz), -14.76 (s, $\Delta\nu_{1/2} = 21$ Hz) were attributed to the bipyridyl groups; one group of two singlets integrating 4 H each at $\delta = -9.70$ (s, $\Delta\nu_{1/2} = 40$ Hz) and $\delta = -3.05$ (s, $\Delta\nu_{1/2} = 22$ Hz) was attributed to the Ar-C*H*$_2$-Ar protons. No correlation was found between the groups of bipyridyl aromatic protons and signals corresponding to the OC*H*$_2$ and C*H*$_3$ groups. Nevertheless, due to their chemical shifts and their integration values, the large singlets found at $\delta = -42.49$ (br. s, $\Delta\nu_{1/2} = 317$ Hz, 4 H) and -22.60 (br. s, $\Delta\nu_{1/2} = 196$ Hz, 6 H) were assigned to the latter, respectively. Finally, the sharp singlet ($\Delta\nu_{1/2} = 4$ Hz) found at $\delta = -1.72$ and integrating 18 H was assigned to two of the four *tert*-butyl groups.

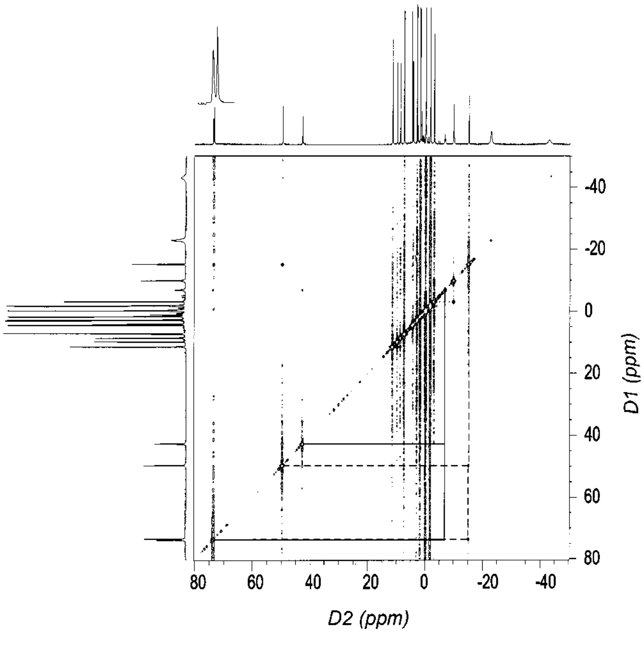

Figure 2. 2D COSY spectrum of cobalt complex **3** (500 MHz, 298 K, CDCl$_3$)

A preliminary study of the complexation of the nickel(II) cation was conducted in solution by UV/Vis titration of **1** with NiCl$_2$·6H$_2$O in CH$_3$CN/CH$_2$Cl$_2$ (95:5) (Figure 3). The new ligand-centred absorption band that appeared at 318 nm upon complexation increased, up to exactly 2 equiv. of the metal ion, confirming the formation of a dinuclear complex. Two close isosbestic points (offset) were observed at 300.5 nm (curves a−d; 0.0−0.8 equiv. of NiCl$_2$·6H$_2$O) and 295.5 nm (curves f−i; 1.2−2.0 equiv. of NiCl$_2$·6H$_2$O), which correspond to the formation of the mono- and the dinuclear species, respectively. Attempts to isolate the former have failed until now.

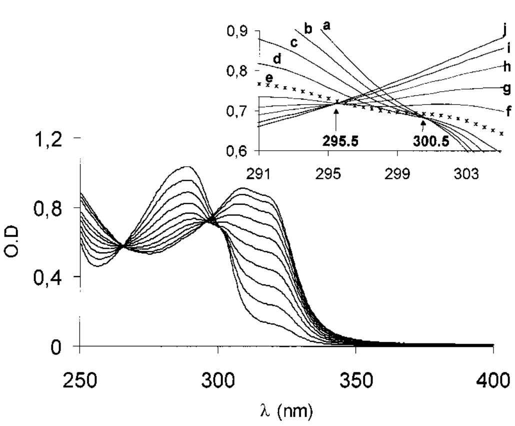

Figure 3. UV/Vis titration of **1** by NiCl$_2$·6H$_2$O [CH$_3$CN/CH$_2$Cl$_2$ (95:5); a−d: 0.0−0.8 equiv. of NiCl$_2$·6H$_2$O; f−i: 1.2−2.0 equiv. of NiCl$_2$·6H$_2$O]

The reaction of **1** with 2 equiv. of NiCl$_2$·6H$_2$O at room temp., followed by evaporation of solvents, re-dissolution in CHCl$_3$ and precipitation with hexane, afforded **4** as a salmon-pink microcrystalline solid. Elemental analysis was consistent with the formula $C_{82}H_{88}Cl_4N_4Ni_2O_4$·0.5CHCl$_3$. Electrospray mass spectrometry (positive mode, 234 V) showed, as for the cobalt complex **3**, the presence of the expected mono-charged species [**1** + 2 NiCl$_2$ − Cl]$^+$ at 1413.5, 1415.5, 1416.5, 1417.5, 1419.5 amu (10%), accompanied by the "decomplexed" species, such as [**1** + NiCl$_2$ − Cl]$^+$ at 1285.5, 1287.5 amu (30%), [**1** + Na]$^+$ at 1216.7 amu (100%), [**1** + H]$^+$ at 1193.7 amu (80%), and by various fragmentation products. Expecting that, as for the cobalt complex **3**, the paramagnetic nature of the nickel(II) ion should only influence the bipyridine unit resonance signals, **4** was analysed by NMR at 500 MHz. The ^{1}H NMR spectrum, recorded in a large frequency domain ($\delta = 0-85$) showed the presence of 18 resonance signals with $\Delta\nu_{1/2}$ varying from 9 to 392 Hz. Among them, two sharp singlets ($\Delta\nu_{1/2} = 9$ Hz) integrating 18 H each at $\delta = 1.97$ and 2.03 were attributed to the *tert*-butyl groups; four singlets integrating 2 H each located at $\delta = 58.22$ ($\Delta\nu_{1/2} = 46$ Hz), 63.80 ($\Delta\nu_{1/2} = 38$ Hz), 80.41 ($\Delta\nu_{1/2} = 80$ Hz), and 84.72 ($\Delta\nu_{1/2} = 90$ Hz) were suspected to be bipyridyl resonance signals. A 2D COSY experiment (Figure 4) confirmed this hypothesis, allowing us to build in two groups of three singlets at $\delta = 84.72$ ($\Delta\nu_{1/2} = 90$ Hz), 58.22 ($\Delta\nu_{1/2} = 46$ Hz), 16.75 ($\Delta\nu_{1/2} = 87$ Hz), and $\delta = 80.41$ ($\Delta\nu_{1/2} = 80$ Hz), 63.80 ($\Delta\nu_{1/2} = 38$ Hz), 22.50 ($\Delta\nu_{1/2} = 26$ Hz). Another correlation was found between two signals located at $\delta = 10.75$ (s, $\Delta\nu_{1/2} = 57$ Hz) and 5.60 (s, $\Delta\nu_{1/2} = 50$ Hz), integrating 4 H each, which were attributed to the Ar-CH_2-Ar groups (Figure 4, offset). The residual signals were not precisely assigned.

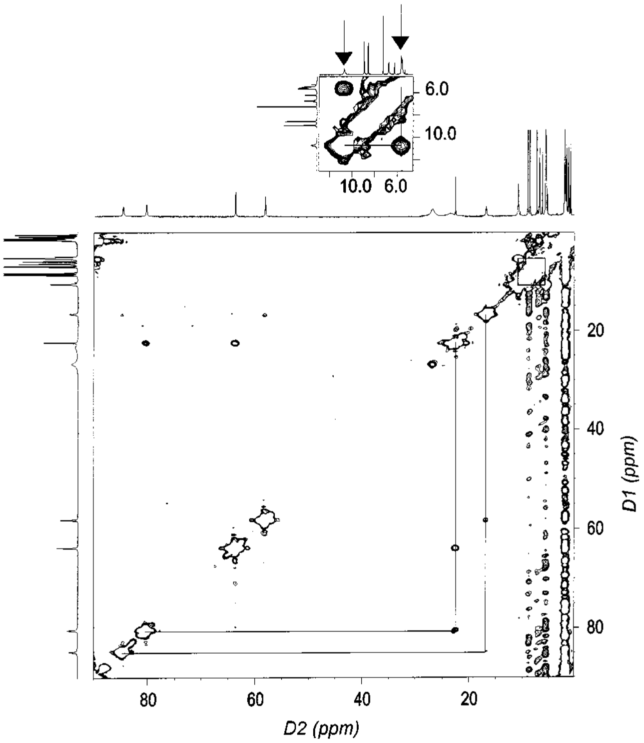

Figure 4. 2D COSY spectrum of nickel complex **4** (500 MHz, 298 K, $CDCl_3$)

Since zinc(II) accepts a tetrahedral geometry with 6,6′-dimethyl-2,2′-bipyridine,[10] we attempted to prepare the dinuclear complex **5**, in which, as for its cobalt and nickel parents **3** and **4**, each metallic centre should be coordinated to one bipyridine unit and to two chloride ions. The complexation of $ZnCl_2$ by ligand **1** was studied by UV/Vis titration, which showed the presence of two close isosbestic points at 299.4 and 303 nm. The two new ligand-centred absorption bands that appeared at 310 and 321 nm upon addition of $ZnCl_2$ increased, up to exactly 2 equiv. of metal ion, confirming the formation of the expected dinuclear species **5**. The latter was prepared as a white microcrystalline solid by mixing the ligand **1** and an excess of $ZnCl_2$ in MeOH and CH_2Cl_2 at room temp., followed by filtration of unchanged $ZnCl_2$ and slow concentration of the filtrate. Surprisingly, with regards to complexes **3** and **4**, electrospray mass spectrometry (positive mode, 80 V) gave poor information on the complex composition, with the presence of one partially "decomplexed" species at 1255.8, 1258.7, and 1259.8 amu [**1** + Zn^{2+} − H^+]$^+$, and the presence of a fragment of ligand at 1032.9, 1033.8, and 1034.9 amu [**1** − 2 ($CH_2C_6H_5$) + Na^+]$^+$. Elemental analysis was consistent with the formula $C_{82}H_{88}Cl_4N_4O_4Zn_2$·$0.5CH_2Cl_2$. Due to its diamagnetism, complex **5** gave a perfectly well-resolved ^{1}H NMR spectrum (Figure 1) between δ = 0 and 10, displaying notably an AB system at δ = 3.12, 4.48 (J_{AB} = 12.9 Hz) assigned to the Ar-CH_2-Ar groups. Both benzyl and bipyridyl methylene groups appear as singlets at δ = 5.02 and 5.81, respectively, indicating the absence of conformational constraint on these pendant arms. All the resonance signals were attributed with the help of a COSY experiment. ^{13}C NMR Ar-CH$_2$-Ar resonance signal was found at δ = 31.56, in the range accepted for the cone conformation.[11]

With the aim of preparing a mononuclear zinc(II) complex displaying structural features equivalent to the abovementioned copper(I) and silver(I) complexes **2** and **B**, we changed the chloride ions to the noncoordinating trifluoromethanesulfonate ion. UV/Vis titration of **1** by $Zn(Tfo)_2$ (Tfo = $CF_3SO_3^-$) in CH_2Cl_2 resulted in the bathochromic shift of the ligand-centred transition from 288 to 317 nm, and confirmed the formation of the expected mononuclear species. Complex **6** was thus prepared by mixing **1** and 1 equiv. of $Zn(Tfo)_2$ in CH_2Cl_2 and methanol at room temperature. Evaporation of the solvents and dissolution of the residue in $CHCl_3$, followed by filtration and addition of hexane afforded **6** as a white precipitate, in a yield of 90%. Electrospray mass spectrometry (positive mode, alcohol-free CH_2Cl_2, +90 V) showed the presence of the expected mono-charged mononuclear species at 1405.7, 1409.6, 1410.7, and 1413.9 amu ([**1** + Zn + Tfo]$^+$), accompanied by a fragment resulting from the loss of one $C_6H_5CH_2O$ group at 1301.8, 1303.8, 1304.8, and 1306.8 amu ([**1** + Zn + Tfo − $C_6H_5CH_2O$ + H]$^+$); working at a lower voltage (45 V) resulted in the appearance of a base peak at 628.5, 629.4, and 630.0 amu attributed to the doubly-charged species ([**1** + Zn]$^{2+}$/2. Elemental analysis was consistent with the formula $C_{82}H_{88}N_4O_4$·$(CF_3SO_3)_2$·Zn·$CHCl_3$. The two Ar-CH$_2$-Ar ^{13}C NMR resonance signals located at δ = 32.37 and 32.87 indicated that **6** was in a distorted cone conformation.[11] A ^{1}H NMR 2D COSY experiment allowed the full assignment of the resonance signals of **6**. As for the tetrahedral species **2** and **B** (Figure 1), the Ar-CH_2-Ar resonance signals appear as two AB systems at δ = 2.67, 3.40 and 2.84, 4.02, indicating a distortion of the conic calixarene platform; the benzyl methylene groups also appear as an AB system at δ = 4.06, 4.21, resulting from an environmental difference generated by the helicoidal complex substructure. The latter is also characterised by a strong AB system located at δ = 5.55, 5.78, attributed to the OCH_2-bpy groups. All attempts to obtain crystals suitable for a convenient X-ray analysis have failed until now.

In parallel, attempts to prepare, on the base of the results obtained with zinc(II), the mononuclear cobalt(II) and nickel(II) species by anion metathesis were unsuccessful.

On the other hand, the different experiments performed to obtain a di- or mononuclear copper(II) complex species resulted in the slow partial to full formation of red copper(I) species. This phenomenon had been previously observed, but as a spontaneous reaction, during the study of **A**[8] and was explained by an oxido reduction process involving an oxidisable substrate and a base in the presence of copper(II) and the bipyridyl calixarene podand. This particular reactivity is currently under investigation.

3. X-ray Crystal Structure Analyses

At the end of the above-mentioned investigations developed in solution, we obtained single crystals suitable for X-ray analysis with the dinuclear cobalt, nickel and zinc complexes **3**, **4** and **5**. In each case the results of the X-ray crystal structure analyses confirmed that two divalent metal ions are complexed by a podand unit in the expected, more or less distorted, tetrahedral mode,[4f,10] with the participation of the two nitrogen atoms of each bipyridine unit and two coordinating chloride ions.

The study of the calixarene platform subunit shows that the three compounds display a similar cone conformation. The inclination angles versus the mean plane of the methylene groups are very similar: two of the phenolic rings are near 90° (values between 90.8 and 98.5°) and the two others carrying the bipyridine units lie outside (values between 129.9 and 135.7°; Figure 5, ORTEP view of nickel complex **4**).

The bipyridine units are very planar (χ^2 from 0.01 to 0.08), but the angles between their planes are different, increasing from 24.8(1)° for **3**, to 31.65(7)° for **5** and 47.39(9)° for **4**. Distances from the metal ion to the mean plane of each bipyridine unit vary from 0.006 Å to 0.103 Å, while the chloride distances vary from 1.626 Å to 2.311 Å.

Distances and angles have been calculated around each metal ion (Tables 1 and 2). The geometry is very similar with a mean angle value N−metal−N of 81.6°. Mean distances metal−N have values of 2.033 Å in **3**, 2.005 Å in **4** and 2.050 Å in **5**, while the mean value for metal−Cl is 2.21 Å for the 3 compounds.

Comparison of cobalt complex subunits in **C** and **3** shows a high similarity in the coordination mode; in **3**, the Co1 coordination appears less distorted than that of Co2 and that in **C**. A similar difference in distortion is also observed between the two complex subunits in **4** and in **5**.

In each compound, one of the benzyl groups (E) is always found in the same position, in such a way that the benzene ring is almost parallel to the corresponding phenolic ring of the calixarene. The second benzyl group (F) is oriented out of the cone (Figure 6).

In the study of the packing of the zinc complex **5**, we can note some $\pi-\pi$ interactions between one ring of a bipyridine unit (B) and another one (D) of the macrocycle obtained by a 2_1 axis (Figure 7). The same situation is found in **3**.

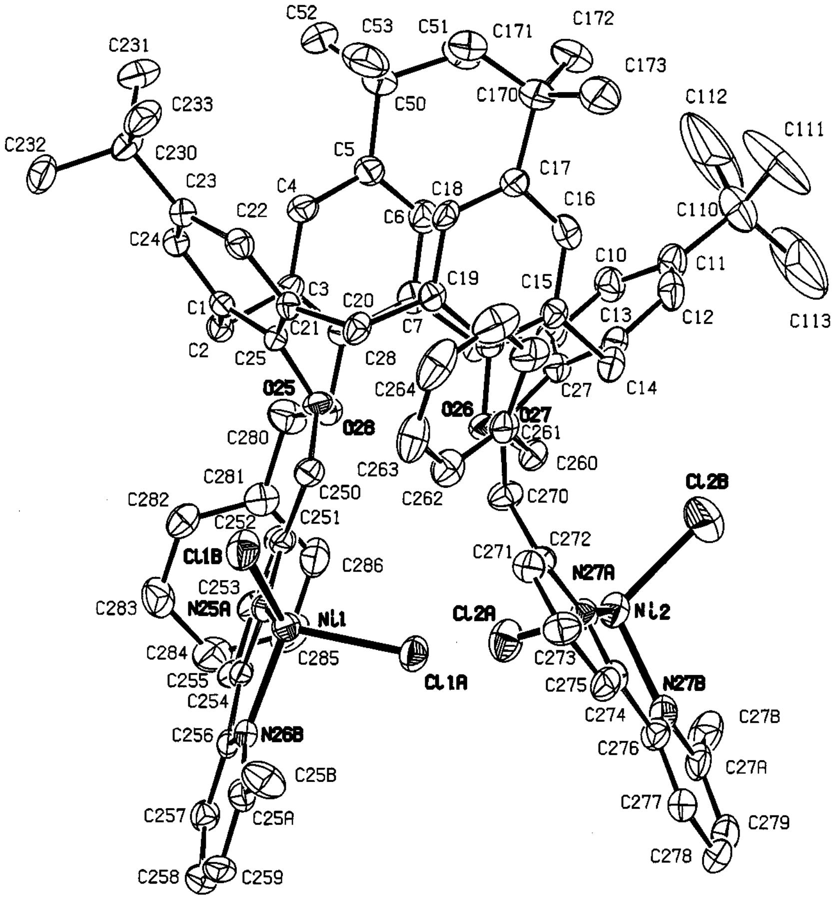

Figure 5. ORTEP side-view and numbering scheme of complex **4** (carbon atoms 8, 9, 26, 225 and 226 are omitted for clarity)

Table 1. Selected geometric parameters around the cobalt centres in complexes **C** and **3**

C		**3**			
Bond angles [°]					
Cl2−Co−Cl3	118.4(9)	Cl10−Co1−Cl11	115.2(9)	Cl20−Co2−Cl21	119.3(1)
N52−Co−N6	182.3(2)	N27M−Co1−N27F	82.3(3)	N25B−Co2−N25M	80.8(3)
N52−Co−Cl2	119.6(2)	N27M−Co1−Cl11	114.4(2)	N25B−Co2−Cl20	119.2(2)
N52−Co−Cl3	108.7(2)	N27F−Co1 −Cl11	111.7(2)	N25B−Co2−Cl21	113.9(2)
N61−Co−Cl2	112.0(2)	N27M−Co1−Cl10	116.0(2)	N25M−Co2−Cl20	110.1(2)
N61−Co−Cl3	110.1(2)	N27F−Co1−Cl10	112.9(2)	N25M−Co2−Cl21	115.3(2)
Bond lengths [Å]					
Co−Cl2	2.2213(2)	Co1−Cl11	2.201(2)	Co2−Cl20	2.210(3)
Co−Cl3	2.222(2)	Co1−Cl10	2.225(2)	Co2−Cl21	2.212(3)
Co−N52	2.021(5)	Co1−N27F	2.029(6)	Co2−N25M	2.050(7)
Co−N61	2.027(6)	Co1−N27M	2.015(6)	Co2−N25B	2.036(6)

Table 2. Selected geometric parameters around the metal centres in complexes **4** and **5**

4		**5**	
Bond angles [°]			
Cl1B−Ni1−Cl1A	118.6(5)	Cl3−Zn1−Cl4	116.95(5)
N26B−Ni1−N25A	82.0(2)	N261−Zn1−N266	81.6(2)
N26B−Ni1−Cl1B	126.7(1)	N261−Zn1−Cl4	114.9(1)
N25A−Ni1−Cl1B	123.1(1)	N261 −Zn1−Cl3	110.7(1)
N26B−Ni1−Cl1A	98.0(1)	N266−Zn1−Cl4	120.9(1)
N25A−Ni1−Cl1A	100.1(1)	N266−Zn1−Cl3	106.5(1)
Cl2B−Ni2−Cl2A	133.0(7)	Cl5−Zn2−Cl6	118.01(6)
N27B−Ni2−N27A	82.1(2)	N281−Zn2−N286	80.9(2)
N27B−Ni2−Cl2B	110.5(1)	N281−Zn2−Cl6	105.7(1)
N27A−Ni2−Cl2B	109.2(1)	N281−Zn2−Cl5	116.4(1)
N27B−Ni2−Cl2A	105.3(1)	N286−Zn2−Cl6	113.6(1)
N27A−Ni2−Cl2A	104.9(1)	N286−Zn2−Cl5	116.2(1)
Bond lengths [Å]			
Ni1−Cl1A	2.240(1)	Zn1−Cl3	2.222(1)
Ni1−Cl1B	2.180(2)	Zn1−Cl4	2.196(1)
Ni1−N25A	2.010(4)	Zn1−N261	2.051(4)
Ni1−N26B	2.003(4)	Zn1−N266	2.038(4)
Ni2−Cl2A	2.228(1)	Zn2−Cl5	2.204(2)
Ni2−Cl2B	2.188(2)	Zn2−Cl6	2.236(2)
Ni2−N27A	2.002(4)	Zn2−N281	2.070(4)
Ni2−N27B	2.003(4)	Zn2−N286	2.041(4)

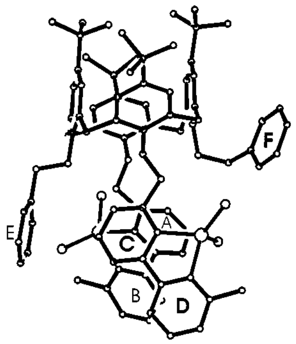

Figure 6. Side views of complex **4** and labelling of pendant bipyridyl and benzyl arms[14]

The nickel complex **4**, which crystallises in the triclinic system, shows interactions between bipyridine units A and B on one part, and pyridine rings C and D on another part.

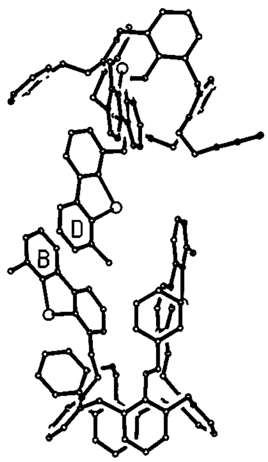

Figure 7. Interactions between rings B and D in complex **5** (*tert*-butyl groups and chlorine atoms were omitted for clarity

The corresponding calixarenes are obtained both by the centre of symmetry and by translation along *b* axis (Figure 8).

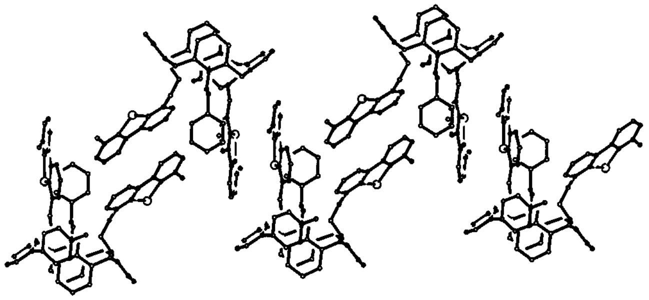

Figure 8. Interactions between the bipyridine units A and B, and C and D in nickel complex **4** (solvent atoms, *tert*-butyl groups and chlorine atoms are omitted for clarity)

Each complex crystallises with solvents which are not shown in the figures: **4** with three molecules of toluene, **3** with one molecule of dichloromethane, and **5** with two molecules of dichloromethane and two of ethanol. For the latter, one of the ethanol molecules displays a short contact with a chlorine atom of one dichloromethane molecule (Cl···O = 3.208 Å).

Conclusion

The bipyridyl-containing calix[4]arene podand **1** described in this report shows interesting versatile complexing properties towards various common transition metal cations, giving in all cases complexes with tetrahedral coordination geometry. Depending on the nature of the cation, but also of the coordinating ability of the counter-anion, these complexes are of the L/M or L/M_2 stoichiometry, as demonstrated by UV/Vis spectroscopy, high resolution NMR spectroscopy and X-ray diffraction analysis. This versatile behaviour is currently the subject of competitive extraction studies, which necessitates developing in parallel the synthesis of the corresponding heterodinuclear complexes.

Experimental Section

General: Melting points (°C, uncorrected values) were determined with an Electrothermal 9100 (capillary apparatus). ^{1}H and ^{13}C NMR spectra were recorded with a Bruker AM 300 or DRX 300 and DRX 500 ($CDCl_3$, TMS as internal standard, chemical shifts in ppm). Mass spectra (electrospray, ES) were recorded with a Platform Micromass apparatus at the Service Central d'Analyse du CNRS, Solaize. Infrared spectroscopy was performed with a Mattson 5000 FT apparatus (KBr, ν in cm^{-1}) and UV spectra were recorded with a Shimadzu UV 2401 PC or a SAFAS UV mc^2 apparatus, λ_{max} in nm, ε in $dm^3 \cdot mol^{-1} \cdot cm^{-1}$. Elemental analyses were performed at the Service Central de Microanalyse, Ecole Supérieure de Chimie, Montpellier. Macherey−Nagel TLC plates were used for chromatography analysis (SiO_2, Polygram SIL G/UV254, ref. no. 805021). All commercially available products were used without further purification unless otherwise specified.

Mononuclear Copper(I) Hexafluorophosphate Complex 2: A solution of 0.0156 g of $Cu(CH_3CN)_4PF_6$ ($4.2\ 10^{-5}$ mol) in 5 mL of acetonitrile was added to a suspension of 0.05 g of **1** ($4.2\ 10^{-5}$ mol) in 20 mL of acetonitrile. Upon complexation, **1** was dissolved, giving an orange-coloured solution. The solvent was evaporated to dryness and the residue was chromatographed (Al_2O_3, CH_2Cl_2) to give **2** (0.055 g, 90%). Orange powder. M.p. 308 °C. IR: $\tilde{\nu}$ = 1570 (C−N), 2960 (C−H). UV/Vis (CH_2Cl_2): λ = 266 (29900), 302 (34700), 447 (5500, MLCT). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.76 (s, 18 H, *Me*$_3$C), 1.34 (s, 18 H, *Me*$_3$C), 1.85 (s, 6 H, *Me*bpy), 2.58, 3.75 ("q", AB, J_{AB} = 13.3, 4 H, Ar-C*H*$_2$-Ar), 2.78, 3.53 ("q", AB, J_{AB} = 12.6, 4 H, Ar-C*H*$_2$-Ar), 3.82, 4.01 ("q", AB, J_{AB} = 11.5, 4 H, OC*H*$_2$C$_6$H$_5$), 5.00, 6.35 ("q", AB, J_{AB} = 12.9, 4 H, OC*H*$_2$bpy), 6.22, 6.30 (AB, J_{AB} = 2.0, 4 H, Ar*H*), 6.47 (dd, *J* = 7.7 *J* = 1.4, 4 H, C$_6$*H*$_5$), 7.02, 7.09 (AB, J_{AB} = 2.0, 4 H, Ar*H*), 7.06−7.29 (m, 6 H, C$_6$*H*$_5$), 7.39 (d, *J* = 7.7, 4 H, bpy), 7.93 (t, *J* = 8.1, 2 H, bpy), 8.16 (t, *J* = 8.1, 2 H, bpy), 8.19 (d, *J* = 8.1, 2 H, bpy), 8.44 (d, *J* = 8.1, 2 H, bpy). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 23.7 (*Me*bpy), 31.8, 32.4 (Ar-*C*H$_2$-Ar), 31.1, 31.7 (*Me*$_3$C), 33.6, 34.2 (Me$_3$*C*), 77.4 (O*C*H$_2$C$_6$H$_5$), 79.3 (O*C*H$_2$bpy), 119.8, 121.9, 124.1, 124.54, 125.50, 126.7, 126.9, 127.8, 127.9, 128.9, 138.7, 139.0 (aromatic *C*H), 131.1, 131.4, 134.8, 135.8, 137.0, 144.5, 145.9, 151.96, 151.98, 152.1, 154.0, 157.7, 157.8 (aromatic *C*). ES-MS (pos. mode): *m*/*z* = 1255.6 [**1** + Cu^I]$^+$. $C_{82}H_{88}CuF_6N_4O_4P \cdot 0.8CH_2Cl_2$ (1470.09): calcd. C 68.30, H 6.08, N 3.77; found C 68.06, H 6.03, N 3.86.

Dinuclear Cobalt(II) Chloride Complex 3: A solution of 0.016 g of $CoCl_2$ ($1.26\ 10^{-4}$ mol) in 5 mL of acetonitrile was added to a solution of 0.05 g of **1** ($4.2\ 10^{-5}$ mol) in 10 mL of CH_2Cl_2. The resulting blue-green solution was stirred at room temp. during 1 h and then concentrated to dryness. The residue was treated with 5 mL of CH_2Cl_2 and the excess of $CoCl_2$ was removed by filtration. Slow concentration of the filtrate gave blue-green crystals of **3** (0.060 g, 98%). M.p. 235 °C. IR: $\tilde{\nu}$ = 1570, 1601 (C−N), 2956 (C−H). UV/Vis (CH_2Cl_2): λ = 317 (30700), 568 (550), 658 (1000). ^{1}H NMR (500 MHz, $CDCl_3$): δ = −42.49 (br. s, $\Delta\nu_{1/2}$ = 317 Hz, 4 H, OC*H*$_2$bpy), −22.60 (br. s, $\Delta\nu_{1/2}$ = 196 Hz, 6 H, *Me*bpy), −14.76 (s, $\Delta\nu_{1/2}$ = 21 Hz, 2 H, bpy), −9.70 (s, $\Delta\nu_{1/2}$ = 40 Hz, 4 H, 2 Ar-C*H*$_2$-Ar), − 6.75 (s, $\Delta\nu_{1/2}$ = 77 Hz, 2 H, bpy), −3.05 (s, $\Delta\nu_{1/2}$ = 22 Hz, 4 H, 2 Ar-C*H*$_2$-Ar), −1.72 (s, $\Delta\nu_{1/2}$ = 4 Hz, 18 H, *Me*$_3$C), −0.13 (s, $\Delta\nu_{1/2}$ = 6 Hz, 18 H, *Me*$_3$C), 1.75 (s, $\Delta\nu_{1/2}$ = 6 Hz, 4 H, Ar*H*), 1.78 (s, $\Delta\nu_{1/2}$ = 6 Hz, 4 H, Ar*H*), 4.17 (s, $\Delta\nu_{1/2}$ = 18 Hz, 4 H, 2 OC*H*$_2$C$_6$H$_5$), 8.63 (s, $\Delta\nu_{1/2}$ = 22 Hz, 4 H, C$_6$*H*$_5$), 9.77 (s, $\Delta\nu_{1/2}$ = 12 Hz, 2 H, C$_6$*H*$_5$), 11.38 (s, $\Delta\nu_{1/2}$ = 22 Hz, 4 H, C$_6$*H*$_5$), 42.28 (s, $\Delta\nu_{1/2}$ = 34 Hz, 2 H, bpy), 49.18 (s, $\Delta\nu_{1/2}$ = 28 Hz, 2 H, bpy), 72.72 (s, $\Delta\nu_{1/2}$ = 25 Hz, 2 H, bpy), 72.93 (s, $\Delta\nu_{1/2}$ = 32 Hz, 2 H, bpy). ES-MS (pos. mode, 252 V): *m*/*z* = 1417.5 [**1** + 2 ($CoCl_2$) − Cl^-]$^+$, 1288.5 [**1** + $CoCl_2$ − Cl^-]$^+$, 1215.7 [**1** + Na]$^+$, 1193.7 [**1** + H]$^+$. $C_{82}H_{88}Cl_4Co_2N_4O_4$ (1453.32): calcd. C 67.77, H 6.10, N 3.86; found C 68.00, H 6.25, N 3.65.

Dinuclear Nickel(II) Chloride Complex 4: A solution of 0.020 g of **1** ($1.67\ 10^{-5}$ mol) and 0.0081 g of $NiCl_2 \cdot 6H_2O$ ($3.35\ 10^{-5}$ mol) in a mixture of CH_2Cl_2 (1 mL), acetonitrile (10 mL) and methanol (1 mL) was stirred at room temp. during 1 h. The resulting salmon-pink solution was concentrated to dryness; the residue was dissolved in $CHCl_3$ and the addition of 10 mL of hexane resulted in the precipitation of **4** as a pink microcrystalline solid (0.017 g; 71%). M.p. 295 °C. IR: $\tilde{\nu}$ = 2957 (CH), 1574, 1603 (C−N). UV/Vis (CH_2Cl_2): λ = 310 (40200), 488 (325). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.97 (s, $\Delta\nu_{1/2}$ = 9 Hz, 18 H, *Me*$_3$C), 2.03 (s, $\Delta\nu_{1/2}$ = 9 Hz, 18 H, *Me*$_3$C), 5.60 (s, 4 H, Ar-C*H*$_2$-Ar), 10.75 (s, $\Delta\nu_{1/2}$ = 57 Hz, 4 H, Ar-C*H*$_2$Ar), 16.75 [s, $\Delta\nu_{1/2}$ = 87 Hz, 2 H, bpy(1)], 22.50 [s, $\Delta\nu_{1/2}$ = 26 Hz, 2 H, bpy(2)], 58.22 [s, $\Delta\nu_{1/2}$ = 46 Hz, 2 H, bpy(1)], 63.80 [s, $\Delta\nu_{1/2}$ = 38 Hz, 2 H, bpy(2)], 80.41 [s, $\Delta\nu_{1/2}$ = 80 Hz, 2 H, bpy(2)], 84.72 [s, $\Delta\nu_{1/2}$ = 90 Hz, 2 H, bpy(1)],1.72 (s, $\Delta\nu_{1/2}$ = 28 Hz, 6 H), 5.32 (s, 4 H), 5.67 (s, 4 H), 6.25 (s, $\Delta\nu_{1/2}$ = 16 Hz, 2 H), 6.77 (s, $\Delta\nu_{1/2}$ = 28 Hz, 4 H), 8.60 (s, $\Delta\nu_{1/2}$ = 14 Hz, 4 H), 8.94 (s, $\Delta\nu_{1/2}$ = 12 Hz, 4 H), 26.82 (s, $\Delta\nu_{1/2}$ = 392 Hz, 4 H) (*Me*bpy, OC*H*$_2$C$_6$H$_5$, C$_6$*H*$_5$, Ar*H*, OC*H*$_2$bpy). ES-MS (pos. mode, 234 V): *m*/*z* = 1417.5 [**1** + 2 ($NiCl_2$) − Cl^-]$^+$, 1287.5 [**1** + ($NiCl_2$) − Cl^-]$^+$, 1215.7 [**1** + Na]$^+$. $C_{82}H_{88}Cl_4N_4Ni_2O_4 \cdot 0.5CHCl_3$ (1512.52): calcd. C 65.51, H 5.90, N 3.70; found C 65.48, H 6.15, N 3.64.

Dinuclear Zinc(II) Chloride Complex 5: A solution of 0.030 g of $ZnCl_2$ ($22.0\ 10^{-5}$ mol) in 5 mL of methanol was added to a solution of 0.060 g of **1** ($5.0\ 10^{-5}$ mol) in 10 mL of CH_2Cl_2. The solution was stirred at room temp. during 1 h, and the excess of $ZnCl_2$ which precipitated was removed by filtration. Slow concentration of the filtrate afforded **5** as white crystals (0.068 g, 90%). M.p. 245 °C. IR: $\tilde{\nu}$ = 1576, 1601 (C−N). UV/Vis (CH_2Cl_2): λ = 321 (32400), 310 (36500). ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 0.93 (s, 18 H, *Me*$_3$C), 1.38 (s, 18 H, *Me*$_3$C), 3.05 (s, 6 H, *Me*bpy), 3.12, 4.48 ("q", AB, J_{AB} = 12.9, 8 H, Ar-C*H*$_2$-Ar), 5.02 (s, 4 H, OC*H*$_2$C$_6$H$_5$), 5.81 (s, 4 H, OC*H*$_2$bpy), 6.60 (s, 4 H, ArH), 7.11−7.22 (m, 10 H, C$_6$*H*$_5$), 7.21 (s, 4 H, ArH), 7.64 (d, *J* = 8.1, 2 H, bpy), 7.67 (d, *J* = 7.4, 2 H, bpy), 7.71 (t, *J* = 7.7, 2 H, bpy), 7.96 (d, *J* = 8.1, 2 H, bpy), 8.11 (t, *J* = 7.9, 2 H, bpy), 9.24 (d, *J* = 7.9, 2 H, bpy). ^{13}C NMR (125.75 MHz, CD_2Cl_2): δ = 24.7 (*Me*bpy), 31.4, 31.8 (Me_3C), 31.6 (Ar-CH_2-Ar), 34.1, 34.4 (Me_3*C*), 75.7 (O$\mathit{CH}_2C_6H_5$), 78.9 (OCH_2bpy), 119.3, 120.0, 125.2, 126.88, 126.94, 127.7, 128.2, 128.4, 130.6, 142.0 (aromatic *C*H), 132.6, 134.9, 137.1, 145.5, 146.9, 147.9, 149.2, 150.7, 154.8, 160.2, 160.9 (aromatic *C*). ES-MS (pos. mode, 80 V): *m*/*z* = 1255.8, 1258.7, 1259.8 [**1** + Zn^{2+} − H^+]$^+$, 1032.9, 1033.8, 1034.9 [**1** − 2 $CH_2C_6H_5$ + Na^+]$^+$. $C_{82}H_{88}Cl_4N_4O_4Zn_2\cdot 0.5CH_2Cl_2$ (1508.69): calcd. C 65.68, H 5.95, N 3.71; found C 65.63, H 6.18, N 3.82.

Mononuclear Zinc(II)trifluoromethanesulfonate Complex 6: A solution of 0.019 g of $Zn(CF_3SO_3)_2$ (5.0 10^{-5} mol) in 10 mL of CH_2Cl_2/methanol was added to a solution of 0.060 g of **1** (5.0 10^{-5} mol) in 20 mL of CH_2Cl_2. The solution was stirred at room temp. during 1 h, and the solvent was evaporated to dryness. The residue was dissolved in 4 mL of $CHCl_3$ and 20 mL of hexane was added, affording **6** as a white precipitate (0.076 g, 90%). M.p. 202 °C. UV/Vis (CH_2Cl_2): λ = 317 (31700). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.76 (s, 18 H, Me_3C), 1.34 (s, 18 H, Me_3C), 1.91 (s, 6 H, *Me*bpy), 2.67, 3.40 ("q", AB, J_{AB} = 12.9, 4 H, Ar-CH_2-Ar), 2.84, 4.02 ("q", AB, J_{AB} = 13.6, 4 H, Ar-CH_2-Ar), 4.06, 4.21 ("q", AB, J_{AB} = 11.8, 4 H, OC$H_2C_6H_5$), 5.55, 5.78 ("q", AB, J_{AB} = 14.0, 4 H, OCH_2bpy), 6.24 (s, 4 H, Ar*H*), 6.48 (d, *J* = 7, 4 H, C_6H_5), 7.09(s, 4 H, Ar*H*), 7.04−7.17 (m, 6 H, C_6H_5), 7.60 (d, *J* = 7.7, 2 H, bpy), 7.62 (d, *J* = 7.7, 2 H, bpy), 8.18 (t, *J* = 7.9, 2 H, bpy), 8.36 (t, *J* = 7.9, 2 H, bpy), 8.60 (d, *J* = 8.1, 2 H, bpy), 8.81 (d, *J* = 8.1, 2 H, bpy). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 23.7 (*Me*bpy), 31.4, 32.0 (Me_3C), 32.4, 32.9 (Ar-CH_2-Ar), 33.9, 34.6 (Me_3*C*), 78.1 (O$\mathit{CH}_2C_6H_5$), 78.2 (OCH_2bpy), 122.2, 124.4, 124.6, 125.0, 126.2, 128.0, 128.5, 128.6, 128.8, 129.2, 129.5, 130.0, 144.1, 144.6 (aromatic *C*H), 128.05, 128.2, 131.2, 131.3, 134.8, 135.8, 136.8, 145.3, 147.1, 148.9, 149.6, 152.0, 153.7, 159.9, 161.0 (aromatic *C*). ES-MS (pos. mode, 90 V): *m*/*z* = 1405.7, 1409.6, 1410.7, 1413.9 [**1** + $Zn(Tfo)_2$ − Tfo^-]$^+$; (45 V): *m*/*z* = 628.5, 629.4, 630.0 [**1** + Zn]$^{2+}$/2. $C_{84}H_{88}F_6N_4O_{10}S_2Zn\cdot CHCl_3$ (1676.55): calcd. C 60.89, H 5.35, N 3.34; found C 60.80, H 5.62, N 3.38.

X-ray Crystallographic Study of Complexes 3, 4 and 5: The data were collected with a Nonius Kappa CCD diffractometer using monochromated Mo-K_α radiation. Structures were solved by direct methods and refined using full-matrix least squares with SHELXS97 [12] and SHELXL97 programmes.[13] All non-H atoms were refined anisotropically. Hydrogen atoms were calculated at their idealised positions and refined isotropically riding on previous atoms. Details for the experimental conditions, cell data, structure and refinement data are given in Table 3. CCDC-167144 (**3**), -167143 (**4**) and -167145 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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Table 3. Crystal data and structure refinement of **3**, **4** and **5**

	3	**4**	**5**
Empirical formula	$C_{83}H_{90}Cl_{8.5}Co_2N_4O_4$	$C_{103}H_{112}Cl_9N_4O_4Ni_2$	$C_{87}H_{102}Cl_7N_4O_6Zn_2$
Formula mass	1538.15	1729.19	1685.63
Temperature [K]	293	293	123
Crystal system, space group	monoclinic, *C*2/*c*	triclinic, $P\bar{1}$	monoclinic, *C*2/*c*
Unit cell dimensions			
a [Å]	45.852(9)	11.691(2)	48.501(9)
b [Å]	15.054(3)	17.225(3)	14.798(3)
c [Å]	23.798(5)	24.510(5)	24.082(5)
α [°]	90	92.94(3)	90
β [°]	91.78(3)	94.08(3)	92.019(3)
γ [°]	90	105.98(3)	90
V [Å ^{3}]	16419(6)	4719.8(16)	17273.2(4)
Z	8	2	8
$D_{calcd.}$ [Mgm^{-3}]	1.244	1.217	1.291
Absorption coefficient [mm^{-1}]	0.648	0.564	0.825
F(000)	804	914	883
Crystal size [mm]	0.35 × 0.30 × 0.25	0.35 × 0.30 × 0.04	0.44 × 0.30 × 0.18
θ range for data collection [°]	2.07 to 25.63	2.83 to 28.16	1.02 to 23.26
Limiting indices	$0 \le h \le 50$	$0 \le h \le 15$	$0 \le h \le 53$
	$0 \le k \le 18$	$-21 \le k \le 21$	$-16 \le k \le 16$
	$-27 \le l \le 27$	$-31 \le l \le 31$	$-26 \le l \le 26$
Reflections collected/unique	12921/12921	18423/18423	117262/12367
Max./min. transmission	0.8547 and 0.8049	0.9778 and 0.8270	0.866 and 0.712
Data/restraints/parameters	12921/0/892	18423/1/1041	12367/2/964
Goodness-of-fit on F^2	0.961	0.952	1.080
Final *R* indices [$I > 2\sigma(I)$]	$R1 = 0.0882$, $wR2 = 0.2433$	$R1 = 0.0748$, $wR2 = 0.1362$	$R1 = 0.0620$, $wR2 = 0.1506$
R indices (all data)	$R1 = 0.1731$, $wR2 = 0.2960$	$R1 = 0.1907$, $wR2 = 0.1669$	$R1 = 0.0798$, $wR2 = 0.1590$
Densities (max./min.) [e·Å^{-3}]	0.894 and −1.084	0.534 and −0.520	1.00 and −0.82

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