

## Polyhedron

### The heterotopic divergent ligand N-oxide-4,4'-bipyridine (bipyMO) as directing-agent in the synthesis of oligo- or polynuclear heterometallic complexes

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#### ABSTRACT

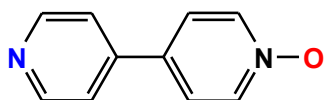
The simple but rarely used heterotopic divergent ligand N-oxide-4,4'-bipyridine (bipyMO) has been exploited, for the first time, for the preparation of heterometallic derivatives, showing the ability to selectively use its two potential coordination sites in dependence of the metal ion nature. By reacting in refluxing acetonitrile  $[\text{Cu}(\text{hfac})_2(\text{bipyMO})]$  with  $[\text{Mn}(\text{hfac})_2(\text{bipyMO})]$  (herein completely characterized), the heterometallic self-assembled monodimensional coordination polymer containing the two regularly alternated moieties  $\text{Cu}(\text{hfac})_2[\text{N}]_2$  and  $\text{Mn}(\text{hfac})_2[\text{O}]_2$  was obtained in high yield and purity and structurally characterized. On the other hand, a molecular heterometallic compound was obtained using, as a ligand, the here prepared mononuclear complex *trans*- $[\text{PtCl}_2(\text{bipyMO})(\text{PPh}_3)]$ , with the hypodentate bipyMO ligand coordinated to platinum through the nitrogen atom. Reaction with  $[\text{Zn}(\text{hfac})_2(\text{DME})]$  afforded the heterometallic trinuclear complex *trans*- $[\text{Zn}(\text{hfac})_2\{\text{trans-PtCl}_2(\text{PPh}_3)(\text{bipyMO})\}_2]$  that was structurally characterized.

*Keywords: divergent ligands, coordination polymers, heterometallic CP, self-assembly, heterometallic complexes, platinum complexes*

#### 1. Introduction

Although 4,4'-bipyridine (bipy) can be considered a classical connector, used in a huge number of *d* metal coordination polymers (CP) [1] and the symmetrically oxidized 4,4'-bipyridine dioxide (bipyDO) has been successfully employed for the CP preparation of the oxophilic lanthanides, [2]

the heterotopic N-oxide-4,4'-bipyridine (bipyMO, Figure 1) has been mostly neglected. Only in a few examples it acts as a bridge between two metal centres with formation of coordination polymers (CP),<sup>[3]</sup> while more often it is coordinated in a hypodentate mode. <sup>[4]</sup> In the latter case the preference to be N- or O-coordinated depends on the metal ion identity and the individual complexes so formed are able to create 2D and 3D networks in the presence of water or other protic species *via* a hydrogen bonding net through the uncoordinated site (O or N, respectively).



**Scheme 1** N-oxide-4,4'-bipyridine (bipyMO)

Among the few examples bipyMO based CPs reported in the literature, Pb(II), [Errore: sorgente del riferimento non trovataa,d] Zn(II) [Errore: sorgente del riferimento non trovatab] and Bi(III) [Errore: sorgente del riferimento non trovatac] ions are involved. It is worth to note that the coordination polymers of lead show alternation of  $\text{PbX}_4[\text{N}]_2$  and  $\text{PbX}_4[\text{O}]_2$  approximately octahedral sites ( $\text{X} = \text{Br}, \text{Cl}, \text{I}, [\text{N}]$  and  $[\text{O}]$  specifying the donor atom of the bridging bipyMO) in a bidimensional extended structure, while in the zinc compound, tetranuclear zinc-arylphosphate building blocks ( $\text{Zn}_4\text{Arphos}_4$ ), with a cubane-like shape, are interconnected by the divergent ligand with the repetition of the  $[(\text{Zn}_4\text{phos}_4)[\text{O}]_2[\text{N}]_2]$  moiety in an extended bidimensional structure.

Complexes where this ligand connects two different metals are missing in the literature.

In this contribution, four isotypical homo-metallic coordination polymers,  $[\text{M}(\text{hfac})_2(\text{bipyMO})]_n$  ( $\text{M} = \text{Zn}, \text{Cu}, \text{Co}, \text{Mn}$ ;  $\text{Hhfac} = 1,1,1,5,5,5$ -hexafluoro-2,4-pentanedione) are described. Every bipyMO ligand bridges two metal centres forming a monodimensional metal-bipyMO network containing two different metal coordination polyhedrons,  $\text{M}(\text{hfac})_2[\text{N}]_2$  and  $\text{M}(\text{hfac})_2[\text{O}]_2$ . Such a result urged us to try the synthesis of transition metal heterometallic species, where metal centres showing a different affinity for nitrogen and oxygen donor ligands could dictate the assembling rules.

## 2. Experimental

### 2.1. Materials and instrumentation

All manipulations were performed under a dinitrogen atmosphere, if not otherwise stated.  $^1\text{H}$ -,  $^{13}\text{C}$ -,  $^{31}\text{P}$ - and  $^{195}\text{Pt}$ -NMR spectra were recorded with a Bruker “Avance DRX400” spectrometer, in  $\text{CDCl}_3$  solution, if not otherwise stated. Chemical shifts were measured in ppm ( $\delta$ ) from TMS by residual solvent peaks for  $^1\text{H}$  and  $^{13}\text{C}$ , from aqueous ( $\text{D}_2\text{O}$ )  $\text{H}_3\text{PO}_4$  (85%) for  $^{31}\text{P}$ , from aqueous

(D<sub>2</sub>O) hexachloroplatinic acid for <sup>195</sup>Pt and from CFC<sub>3</sub> for <sup>19</sup>F. A sealed capillary containing C<sub>6</sub>D<sub>6</sub> was introduced in the NMR tube to lock the spectrometer to the deuterium signal when non-deuterated solvents were used. FTIR spectra in solid phase were recorded with a Perkin–Elmer “Spectrum One” spectrometer, equipped with an ATR accessory. Elemental analyses (C, H, N) were performed at Dipartimento di Scienze e Tecnologie Chimiche, Università di Udine. *Trans*-[Pt(μ-Cl)Cl(PPh<sub>3</sub>)<sub>2</sub>]<sup>[5]</sup> [Cu(hfac)<sub>2</sub>·H<sub>2</sub>O], [Cu(hfac)<sub>2</sub>],<sup>[6]</sup> [Co(hfac)<sub>2</sub>(DME)]<sup>[7]</sup> and bipyMO, [Errore: sorgente del riferimento non trovata] were prepared according to the literature. The following commercial reagents were used as received: ZnO (Sigma Aldrich), Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Carlo Erba), Mn(SO<sub>4</sub>)·6H<sub>2</sub>O (Carlo Erba), Hhfac (Strem Chemicals). Commercial MeCN (BDH), toluene (Sigma Aldrich) and methanol (Aldrich) were used as received, while 1,2-dimethoxyethane, DME, (Acros Organics) was dried according to reported procedures.<sup>[8]</sup>

## 2.2. Synthesis

### 2.2.1. Synthesis of [Zn(hfac)<sub>2</sub>(DME)] (1)

In a 250 mL flask ZnO (0.50 g, 6.14 mmol) were treated with Hhfac (2.94 g, 14.13 mmol) in DME (50 mL). The suspension was stirred for 12 h. A colourless solution was obtained, that was evaporated to dryness under vacuum at room temperature with formation of a colourless solid residue [2.72 g, 77.8 % yield as [Zn(hfac)<sub>2</sub>(DME)]]. Anal. Calc. for ZnC<sub>14</sub>H<sub>12</sub>F<sub>12</sub>O<sub>6</sub>: C, 29.5; H, 2.1; Zn, 11.5. Found: C, 30.0; H, 1.9; Zn, 11.3. ATR FTIR (relevant bands in the range 1700-1100 cm<sup>-1</sup>): 1647m, 1599mw, 1559w, 1532w, 1489m, 1467m, 1252ms, 1198ms, 1140ms cm<sup>-1</sup>. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, ppm): 6.10 (s, CH, 2H), 3.77 (s, CH<sub>2</sub>, 4H), 3.54 (s, CH<sub>3</sub>, 6H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, ppm): 179.9 (q, C=O, 4C, <sup>2</sup>J<sub>C-F</sub> 35 Hz), 117.3 (q, CF<sub>3</sub>, 4C, <sup>1</sup>J<sub>C-F</sub> 285 Hz), 89.5 (s, CH, 2C), 70.6 s (CH<sub>2</sub>, 2C), 60.24 s (CH<sub>3</sub>, 2C).

Nice crystals were obtained by sublimation of the product under vacuum at 60 °C. Single crystals were selected to carry out X-ray diffraction studies. The product can be obtained in higher yields (about 85 %) by using a Hhfac excess. The product must be stored in inert atmosphere to prevent its hydrolysis. It is soluble in MeCN at about 30 °C and sparingly soluble in the common organic solvents.

### 2.2.2. Synthesis of [Mn(hfac)<sub>2</sub>(DME)] (2)

This synthesis is similar to the one previously described for Co(hfac)<sub>2</sub>(DME), [Errore: sorgente del riferimento non trovata] except it was carried out under N<sub>2</sub>. A yellow solid was obtained (2.30 g, 69.6% yield as [Mn(hfac)<sub>2</sub>(DME)]]. Anal. Calc. for MnC<sub>14</sub>H<sub>12</sub>F<sub>12</sub>O<sub>6</sub>: C, 30.1; H, 2.2. Found: C, 30.5; H, 2.2. ATR FTIR (relevant bands in the range 1700-1100 cm<sup>-1</sup>): 1646s, 1601mw, 1558w, 1531w, 1495m, 1254s, 1197ms, 1140ms cm<sup>-1</sup>. Single crystals were obtained by sublimation of the product

under vacuum at 60 °C and X-ray diffraction studies showed the derivative was isotypic with **1**: monoclinic,  $P 2_1/n$ ,  $a=12.039(4)$  Å,  $b=13.326(8)$  Å,  $c=14.201(6)$  Å,  $\beta=100.09(2)^\circ$ . The product must be stored in inert atmosphere to prevent its hydrolysis. It is soluble in MeCN at about 30 °C and sparingly soluble in the common organic solvents.

### 2.2.3. Synthesis of $[\text{Cu}(\text{hfac})_2(\text{bipyMO})]$ (**3**)

$[\text{Cu}(\text{hfac})_2]$  (0.99 g, 1.94 mmol) was added to a suspension of bipyMO (0.36 g, 2.09 mmol) in toluene (50 mL) and the mixture was refluxed for 5 h. Once at room temperature, the green suspension was filtered. The green solid was dried for 10 h under vacuum (1.03 g, 81.7% yield as  $[\text{Cu}(\text{hfac})_2\text{bipyMO}]$ ). Anal. Calc. for  $\text{CuC}_{20}\text{H}_{10}\text{F}_{12}\text{N}_2\text{O}_5$ : C, 37.0; H, 1.5; N, 4.3. Found: C, 37.1; H, 1.3; N: 4.4. FTIR ATR (relevant bands in the range 1700-1100  $\text{cm}^{-1}$ ): 1644s, 1615m, 1597w, 1553m, 1528m, 1489s, 1480s, 1418m, 1343w, 1314d, 1252s, 1219s, 1199s, 1184s, 1139s, 1102s  $\text{cm}^{-1}$ . Similar results were obtained by carrying out the synthesis in MeCN starting from the hydrated reagents  $[\text{Cu}(\text{hfac})_2\cdot\text{H}_2\text{O}]$  and  $[\text{bipyMO}\cdot\text{H}_2\text{O}]$ . After exposition of the sample to the air for long periods, no significant variations in the IR spectrum were observed. After sublimation under vacuum at 140 °C the solid showed an IR spectrum over-imposable to the one of the initial product. The derivative is soluble in refluxing MeCN; a solution, slowly cooled to room temperature, separated out single crystals suitable for X-ray diffraction studies.

### 2.2.4. Synthesis of $[\text{Mn}(\text{hfac})_2(\text{bipyMO})]$ (**4**)

In a Schlenk's tube  $\text{Mn}(\text{hfac})_2(\text{DME})$  (**2**) (0.72 g, 1.29 mmol) was dissolved in MeCN (10 mL) at 30 °C. In the meantime, a suspension of  $\text{bipyMO}\cdot 2\text{H}_2\text{O}$  (0.27 g, 1.30 mmol) in MeCN (30 mL) was prepared in another tube. The former solution was added to the ligand suspension with immediate formation of a clear solution. The solution was refluxed for 2 h and then the suspension was slowly cooled to room temperature and filtered. The orange solid was dried under vacuum at room temperature for about 2 h (0.22 g, 26.6 % yield as  $[\text{Mn}(\text{hfac})_2(\text{bipyMO})]$ ). Anal. Calc. for  $\text{C}_{20}\text{H}_{10}\text{F}_{12}\text{MnO}_5\text{N}_2$ : C, 37.4; H, 1.6; N, 4.4. Found: C, 37.3; H, 1.5; N: 4.0. FTIR ATR (relevant bands in the range 1700-1100  $\text{cm}^{-1}$ ): 1643m, 1615mw, 1598mw, 1557w, 1530w, 1485m, 1417mw, 1250s, 1221s, 1188ms, 1138ms  $\text{cm}^{-1}$ . The filtrate was cooled at -20 °C. After 12 h yellow-brown crystals separated out. The suspension was filtered and the crystals were dried under vacuum at room temperature collapsing to a powder with the same elemental analysis and the same IR spectrum of the former product (0.38 g, 46.0 % yield as  $[\text{Mn}(\text{hfac})_2(\text{bipyMO})]$ , 72.6 % total yield). The product was crystallized from methanol. Single crystals X-ray diffraction studies were carried out.

### 2.2.5. Synthesis of $[\text{Zn}(\text{hfac})_2(\text{bipyMO})]$ (**5**)

In a Schlenk's tube  $\text{Zn}(\text{hfac})_2(\text{DME})$  (**1**) (1.46 g, 2.56 mmol) were dissolved in MeCN (14.5 mL). In the meantime, a suspension of  $\text{bipyMO}\cdot 2\text{H}_2\text{O}$  (0.57 g, 2.74 mmol) in MeCN (60 mL) was prepared

in another tube. The former solution was added to the ligand suspension with immediate formation of a clear solution. After a few minutes the appearance of a solid was observed. The suspension was refluxed under stirring for about 2 h. The majority of the solid phase dissolved. After a slow cooling to room temperature, well formed crystals were obtained. The suspension was filtered and the crystals were dried under vacuum at room temperature for about 2 h (1.23 g, 73.7 % yield as  $[\text{Zn}(\text{hfac})_2(\text{bipyMO})]$ ). Anal. Calc. for  $\text{ZnC}_{20}\text{H}_{10}\text{F}_{12}\text{O}_5\text{N}_2$ : C, 36.8; H, 1.6; N, 4.3. Found: C, 37.1; H, 1.3; N: 4.3. FTIR ATR (relevant bands in the range 1700-1100  $\text{cm}^{-1}$ ): 1645m, 1616mw, 1557w, 1532m, 1498m, 1417w, 1252s, 1220s, 1193s, 1139ms  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  ( $\text{CD}_3\text{CN}$ , ppm): 8.69 (d, NCH, 2H), 8.28 (d, ONCH, 2H), 7.78 (d, NCHCH and ONCHCH, 4H), 6.05 (s,  $\beta$ -diketone CH, 2H).  $^{19}\text{F-NMR}$  ( $\text{CD}_3\text{CN}$ )  $-77.5$  ppm.

X-ray diffraction measurements on the crystals showed the product was isotopic with  $^1[\text{Cu}(\text{hfac})_2(\text{bipyMO})]_{\infty}$ , (3): monoclinic,  $P 2_1/n$ ,  $a=18.787(4)$  Å,  $b=7.515(2)$  Å,  $c=19.543(6)$  Å,  $\beta=117.05(2)^\circ$ .

#### 2.2.6. Synthesis of $^1[\text{Co}(\text{hfac})_2(\text{bipyMO})]$ (6)

In a Schlenk's tube  $[\text{Co}(\text{hfac})_2(\text{DME})]$  (0.70 g, 1.24 mmol) was dissolved in MeCN (16 mL) at 30 °C. In the meantime, a suspension of  $\text{bipyMO}\cdot 2\text{H}_2\text{O}$  (0.27 g, 1.30 mmol) in MeCN (60 mL) was prepared in another tube. The former solution was added to the ligand suspension with the immediate formation of a clear solution. After a few minutes an orange solid precipitated out. The suspension was refluxed for 2 h and then slowly cooled to room temperature. After 12 h the suspension was filtered. The orange solid was dried under vacuum at room temperature for about 2 h. (0.51 g, 63.8% yield as  $[\text{Co}(\text{hfac})_2(\text{bipyMO})]$ ). Anal. Calc. for  $\text{CoC}_{20}\text{H}_{10}\text{F}_{12}\text{O}_5\text{N}_2$ : C, 37.2; H, 1.6; N, 4.3. Found: C, 37.8; H, 1.4; N: 3.8. FTIR ATR (relevant bands in the range 1700-1100  $\text{cm}^{-1}$ ): 1638w, 1556mw, 1529w, 1486w, 1417mw, 1253m, 1218s, 1194m, 1139ms  $\text{cm}^{-1}$ . X-ray diffraction measurements on the crystals showed the product was isotopic with  $^1[\text{Cu}(\text{hfac})_2(\text{bipyMO})]_{\infty}$ , (3): monoclinic,  $P 2_1/n$ ,  $a=18.75(2)$  Å,  $b=7.54(1)$  Å,  $c=19.55(2)$  Å,  $\beta=117.41(4)^\circ$ .

#### 2.2.7. Synthesis of $^1[\text{Cu}(\text{hfac})_2\text{Mn}(\text{hfac})_2(\text{bipyMO})_2]$ (7)

A suspension containing  $^1[\text{Cu}(\text{hfac})_2\text{bipyMO}]$  (3) (170 mg, 0.26 mmol) and  $^1[\text{Mn}(\text{hfac})_2\text{bipyMO}]$  (4) (170 mg, 0.26 mmol) in MeCN (25 mL) was refluxed for 2 h. A solution was obtained that was slowly cooled to room temperature. Greenish crystals separated out that were recovered after filtration and dried under vacuum for 2 h (270 mg, 79.4 % yield as  $[\text{Cu}(\text{hfac})_2\text{Mn}(\text{hfac})_2(\text{bipyMO})_2]$ ). Some crystals were selected for X-ray diffraction studies. Anal. Calc. for  $\text{C}_{40}\text{H}_{20}\text{CuF}_{24}\text{MnN}_4\text{O}_{10}$ : C, 37.2; H, 1.6; N, 4.3. Found: C, 37.5; H, 2.0; N: 4.1. FTIR ATR (relevant bands in the range 1700-1100  $\text{cm}^{-1}$ ): 1645s, 1615m, 1595w, 1553m, 1528m, 1495s, 1486s,

1417m, 1341w, 1252s, 1220s, 1192s, 1184s, 1136s cm<sup>-1</sup>. An identical IR spectrum was observed for crystals obtained by sublimation under vacuum at 140°C.

### 2.2.8. Synthesis of [PtCl<sub>2</sub>(PPh<sub>3</sub>)(bipyMO)] (**8**)

For the experiment carried out in two steps ( $\{[\text{Pt}(\mu\text{-Cl})\text{Cl}(\text{PPh}_3)]_2\text{:bipyMO}\}$  molar ratio 1:1 and 1:2) and monitored by NMR spectroscopy see R&D. In a Schlenk's tube  $[\text{Pt}(\mu\text{-Cl})\text{Cl}(\text{PPh}_3)]_2$  (320 mg,  $3.03 \times 10^{-1}$  mmol) was treated with  $\text{bipyMO}\cdot 2\text{H}_2\text{O}$  (131 mg,  $6.30 \times 10^{-1}$  mmol) in  $\text{CHCl}_3$  (5 mL). The mixture was stirred at room temperature. A yellow solution was initially obtained containing *trans*- $[\text{PtCl}_2(\text{PPh}_3)(\text{bipyMO})]$ , *trans*-**8** (see R&D). By addition of a small excess of bipyMO the solution slowly turned colourless with precipitation of colourless crystals. The suspension was filtered. Some crystals were selected to carry out X-ray diffraction studies, *cis*- $[\text{PtCl}_2(\text{PPh}_3)(\text{bipyMO})\cdot 3\text{CHCl}_3]$ , *cis*-**8** $\cdot 3\text{CHCl}_3$ . The remaining crystals were dried under vacuum at room temperature for about 2 h (480 mg, 90.0 % yield as  $[\text{PtCl}_2(\text{PPh}_3)(\text{bipyMO})]\cdot 1.5\text{CHCl}_3$ ). Anal. Calc. for  $\text{C}_{28}\text{H}_{23}\text{N}_2\text{OPPt}\cdot 1.5\text{CHCl}_3$ : C, 40.3; H, 2.8; N, 3.2. Found: C, 40.8; H, 2.9; N: 3.0. For NMR data see R&D and SI.

### 2.2.9. Synthesis of *trans*[Zn(hfac)<sub>2</sub>{*trans*-PtCl<sub>2</sub>(PPh<sub>3</sub>)(bipyMO)}<sub>2</sub>] (**9**)

$[\text{Pt}(\mu\text{-Cl})\text{Cl}(\text{PPh}_3)]_2$  (32 mg,  $3.0 \times 10^{-2}$  mmol) was reacted in a NMR tube with  $\text{bipyMO}\cdot 2\text{H}_2\text{O}$  (12.5 mg,  $6.0 \times 10^{-2}$  mmol) in  $\text{CDCl}_3$  (0.6 mL) with formation of a yellow solution. The <sup>1</sup>H-NMR spectrum revealed the formation of *trans*- $[\text{PtCl}_2(\text{PPh}_3)(\text{bipyMO})]$ , *trans*-**8**.  $\text{Zn}(\text{hfac})_2(\text{DME})$  (**1**) (17 mg,  $3.0 \times 10^{-2}$  mmol) was added. The solution was analyzed through multinuclear NMR spectroscopy (see R&D). The data were in agreement with the formation of the trinuclear heterometallic product. The solution was evaporated to dryness and the residue was dissolved in toluene. Crystals separated out from the solution by slow diffusion of pentane vapours. Some crystals were selected to carry out X-ray diffraction studies. The remaining crystals were dried under vacuum at room temperature for about 2 h (30 mg, 53.2 % yield as  $[\text{Zn}(\text{hfac})_2\{\text{PtCl}_2(\text{PPh}_3)(\text{bipyMO})\}_2]$ ). For NMR data see R&D and SI.

## 2.3. Crystallographic data collection and refinement

Crystals of **1**, **3**, **4** and **7** were glued at the end of glass fibres and those of *cis*-**8** and **9** were sealed in glass capillaries. The diffractions of all samples were studied at room temperature by means of a Bruker SMART Breeze CCD diffractometer equipped with graphite monochromated Mo-*K*α radiation ( $\lambda = 0.71073$  Å). The crystal data are listed in Tables 1 and 2. The collected intensities were corrected for Lorentz and polarization effects and for absorption through a multi-scan method.

[<sup>9</sup>] All the structure solutions were found by means of the automatic direct methods contained in SHELX97 programme. [<sup>10</sup>] During the refinement several structures showed problems of disorder in CF<sub>3</sub> groups which were treated as distributed in two limit positions. In the crystal structure of

compound **9** the lattice solvent was so disordered that was impossible to find in the difference Fourier map a starting model for inserting it in the refinement procedure. So the SQUEEZE procedure [11] was used for subtracting its contribute to the structure factors.

The final reliability factors obtained at the end of refinement are listed in Tables 1 and 2.

**Table 1.** Crystal data and refinement summaries for **1**, **3**, **4** and **7**.

Identification code	<b>1</b>	<b>3</b>	<b>4</b>	<b>7</b>
CCDC number	1560242	1560243	1560244	1560245
Empirical formula	C <sub>14</sub> H <sub>12</sub> F <sub>12</sub> O <sub>6</sub> Zn	C <sub>20</sub> H <sub>10</sub> F <sub>12</sub> N <sub>2</sub> O <sub>5</sub> Cu	C <sub>20</sub> H <sub>10</sub> F <sub>12</sub> N <sub>2</sub> O <sub>5</sub> Mn	C <sub>40</sub> H <sub>20</sub> F <sub>24</sub> N <sub>4</sub> O <sub>10</sub> CuMn
Formula weight	569.61	649.84	641.24	1291.09
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>a</i> (Å)	12.0103(4)	18.3682(4)	19.6404(6)	18.3844(4)
<i>b</i> (Å)	13.6351(5)	7.7706(2)	7.1436(2)	7.76700(10)
<i>c</i> (Å)	13.8486(5)	19.4086(4)	20.2301(6)	19.1518(4)
$\beta$ (°)	99.351(2)	117.2960(10)	116.3360(10)	116.2010(10)
Volume (Å <sup>3</sup> )	2237.73(14)	2461.76(10)	2543.75(13)	2453.73(8)
<i>Z</i>	4	4	4	2
$\rho_{\text{calc}}$ (g cm <sup>-3</sup> )	1.691	1.753	1.674	1.747
$\mu$ (mm <sup>-1</sup> )	1.223	1.013	0.641	0.841
<i>F</i> (000)	1128	1284	1268	1276
$\theta$ range (°)	2.5 to 31.6	1.3 to 27.5	1.2 to 29.1	2.5 to 25.1
Reflections collected	22171	20336	20556	17400
Independent reflections	6677	5563	6158	4328
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.022	1.093	1.038	1.023
Final <i>R</i> <sub>1</sub> [ <i>I</i> ≥ 2σ( <i>I</i> )]	0.0618	0.0624	0.0618	0.0448
Final <i>wR</i> <sub>2</sub> [ <i>I</i> ≥ 2σ( <i>I</i> )]	0.1568	0.1357	0.1906	0.1071
Final <i>R</i> <sub>1</sub> [all data]	0.1271	0.1244	0.0969	0.0744
Final <i>wR</i> <sub>2</sub> [all data]	0.1956	0.1585	0.2340	0.1637
Largest peak/hole ( <i>e</i> Å <sup>-3</sup> )	0.498, -0.216	0.402, -0.236	0.711, -0.368	0.296, -0.185

**Table 2.** Crystal data and refinement summaries for **8** and **9**.

Identification code	<i>cis</i> - <b>8</b> · 3 CHCl <sub>3</sub>	<b>9</b> · solvent
CCDC number	1560246	1560247
Empirical formula	C <sub>31</sub> H <sub>26</sub> Cl <sub>11</sub> N <sub>2</sub> OPPt	C <sub>66</sub> H <sub>48</sub> Cl <sub>4</sub> F <sub>12</sub> N <sub>4</sub> O <sub>6</sub> P <sub>2</sub> Zn · solv
Formula weight	1058.55	1880.37
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>a</i> (Å)	13.9679(11)	17.3597(13)
<i>b</i> (Å)	17.6369(14)	9.3562(6)
<i>c</i> (Å)	17.5444(13)	43.785(3)
$\beta$ (°)	112.8240(10)	97.154(4)
Volume (Å <sup>3</sup> )	3983.7(5)	7056.3(8)
<i>Z</i>	4	4
$\rho_{\text{calc}}$ (g cm <sup>-3</sup> )	1.765	1.770
$\mu$ (mm <sup>-1</sup> )	4.329	4.573
<i>F</i> (000)	2056	3648
$\theta$ range (°)	2.8 to 27.5	0.9 to 26.5
Reflections collected	35265	55986
Independent reflections	9084	14611
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.059	1.078
Final <i>R</i> <sub>1</sub> [ <i>I</i> ≥ 2σ( <i>I</i> )]	0.0508	0.0694
Final <i>wR</i> <sub>2</sub> [ <i>I</i> ≥ 2σ( <i>I</i> )]	0.1255	0.1470
Final <i>R</i> <sub>1</sub> [all data]	0.0825	0.0995
Final <i>wR</i> <sub>2</sub> [all data]	0.1423	0.1600
Largest peak/hole ( <i>e</i> Å <sup>-3</sup> )	3.123, -1.326	3.034, -4.552

### 3. Results and Discussion

The heterotopic divergent ligand bipyMO is expected to favour self-assembly processes by reaction with complexes having two available binding sites in the metal coordination sphere with production of coordination polymers. We decided to choose the fragment [M(hfac)<sub>2</sub>] (M = Zn, Cu, Co, Mn) as a node to obtain monodimensional coordination polymers, <sup>1</sup><sub>∞</sub>[M(hfac)<sub>2</sub>(bipyMO)], for metal ions usually adopting a coordination number 6, since anionic hfac ligands show a strong preference towards a chelate mode and only two available positions are left. Besides, the chosen precursors, [M(hfac)<sub>2</sub>(DME)<sub>x</sub>] (M = Cu, *x* = 0; M = Zn, Co, Mn, *x* = 1) can be easily prepared, have appreciable volatility and solubility in organic solvents and show a pronounced Lewis acid character of the metal centre due to the electron-withdrawing effect of the β-diketonato CF<sub>3</sub> substituents. Furthermore, we have previously used with success Ln(hfac)<sub>3</sub> nodes to prepare lanthanide CPs with 4,4'-bipyridine exploiting the same synthetic rationale. [12]

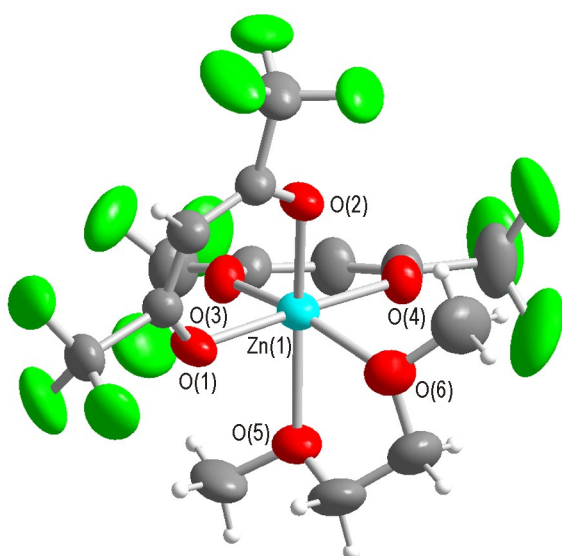
At the best of our knowledge, the zinc and manganese complexes [M(hfac)<sub>2</sub>(DME)] (M = Zn, Mn) were not previously described in the literature except for a patent reporting the zinc derivative as volatile additive for fuel. [13]

We easily obtained **1** by reacting ZnO with Hhfac and DME with a procedure similar to the one described for the preparation of the analogous cadmium complex, [Cd(hfac)<sub>2</sub>(DME)]. [14] In our synthesis DME was used as solvent and a slight excess of β-diketone was added. The manganese species **2** was prepared starting from the freshly precipitated manganese(II) hydroxide in a non-oxidizing atmosphere to prevent manganese oxidation. Also in this case the reaction was carried out



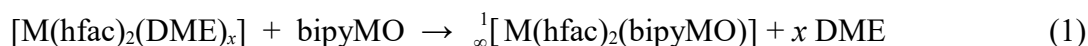
in DME as solvent and an excess of  $\beta$ -diketone was used. Both complexes were purified by sublimation under vacuum at about 60 °C yielding crystals suitable for single crystal X-ray diffraction studies. The IR spectra of the sublimates were identical to the ones of the untreated products.

The molecular structure of **1** is shown in Fig. 1 and selected bond distances are listed in the caption. Two hexafluoroacetylacetonato ligands and one DME are bonded to zinc in an approximately octahedral coordination, similar to the one reported for  $[\text{Co}(\text{hfac})_2(\text{DME})]$ , [Errore: sorgente del riferimento non trovata] and only slightly distorted for the differences in the bite angles and in the Zn–O bond lengths of the ligands (the neutral DME Zn–O distance being slightly longer). Compound **2** is isotopic.



**Figure 1.** Molecular structure of **1**. Bond distances (Å) around Zn atom: Zn(1)–O(1) 2.044(3), Zn(1)–O(2) 2.036(2), Zn(1)–O(3) 2.042(3), Zn(1)–O(4) 2.050(3), Zn(1)–O(5) 2.188(3), Zn(1)–O(6) 2.155(3).

The reactions between the precursors and bipyMO were carried out in 1:1 molar ratio (Eq 1). Initially, the copper derivative,  $[\text{Cu}(\text{hfac})_2]$  and bipyMO were reacted in refluxing toluene in anhydrous conditions with formation of the green product, **3**, that was crystallized from acetonitrile where it is soluble at the reflux temperature. Since no difference was noticed in the outcome of the reaction in the presence of water or other oxygen donor ligands, the monoglyme adducts of zinc, cobalt and manganese and  $\text{bipyMO} \cdot 2\text{H}_2\text{O}$  were, later on, more conveniently used for the preparation of the corresponding CPs.

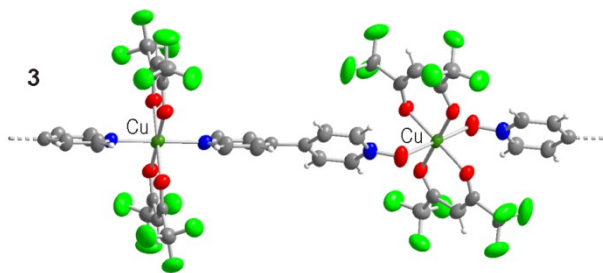


M = Cu, x = 0; M = Zn, Co, Mn, x = 1

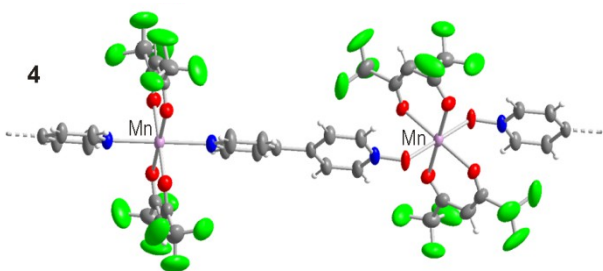
The zinc, cobalt and manganese derivatives **4**, **5** and **6** were synthesized by reacting the monoglyme hexafluoroacetylacetonates [M(hfac)<sub>2</sub>(DME)] with bipyMO in refluxing acetonitrile so obtaining solutions that separated out well formed crystals by cooling to room temperature.

X-Ray diffraction studies showed that the four compounds, **3-6**, were isotypic. Their IR spectra appeared similar.

The molecular and crystal structures of **3** and **4** were solved by single crystal X-Ray diffraction measurements. The molecular structures are shown in Fig. 2 and 3, respectively.



**Figure 2.** Molecular structure of a fragment of the CP  $[\text{Cu}(\text{hfac})_2(\text{bipyMO})]_n$ , **3**.

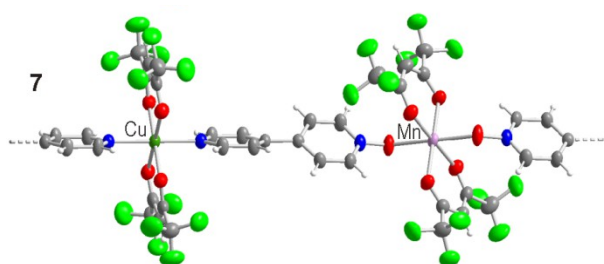


**Figure 3.** Molecular structures of a fragment of the CP  $[\text{Mn}(\text{hfac})_2(\text{bipyMO})]_n$ , **4**.

The bipyMO ligand, having two different ligand sites, may in principle connect the metal centres both in the head-tail-head-tail (N—O—M—N—O—M) or in head-head-tail-tail way (O—N—M—N—O—M—O, N—O representing the bridging bipyMO). In the structure of **3** and **4** we found only the latter arrangement as previously reported for the coordination polymers of Pb(II) [Errore: sorgente del riferimento non trovataa,d] and Bi(III). [Errore: sorgente del riferimento non trovatac] One metal centre binds two N-ends of two bipyMO ligands and the next ones bind two O-ends of two bipyMO ligands with both N—M—N and O—M—O bond angles of 180°. So the metal ions lay on inversion centres that make them perfectly aligned in each chain (spanned by 12.03, 12.14 Å in **3** and **4**, respectively) and make centrosymmetric the two hfac ligands that complete their coordination sphere. Although the metal ions are aligned, the chains appear slightly puckered due to the N—O—M bond angle values of 128.7 and 124.8 degrees in **3** and **4**, respectively. The coordination polyhedrons around the metals are almost ideal octahedral, the principal deviation

being due to the differences between  $M-O_{\text{hfac}}$  and  $M-O_{\text{bipyMO}}$  or  $M-N_{\text{bipyMO}}$  bond lengths. These different lengths and the volumes of each octahedron are reported in Table 3.

The solubility of the coordination polymers **4-6** in hot acetonitrile is probably due to a fragmentation in oligomers favoured by the solvent coordination properties. On this basis it was reasonable to expect that by mixing a couple of homometallic coordination polymers in warm MeCN the system would have had the chance to produce a selectively ordered heterometallic polymer. In fact, three scenarios were expected: a) a statistic distribution of the two different metal sites in a heterometallic species, b) the retention of the original mixture of the two homometallic coordination polymers, c) the self-assembly of an ordered coordination polymer with regularly alternated  $[M(\text{hfac})_2]O_2$  and  $[M'(\text{hfac})_2]N_2$  sites. It is reasonable to suppose that the last arrangement is favoured when the two metal ions show different affinity for N- or O-donor ligands, as previously suggested by Loeb and co-workers [Errore: sorgente del riferimento non trovataa] and by Mercier and co-workers.[Errore: sorgente del riferimento non trovataa] Although we were aware of the remarkable complexity of a self-assembly process of heterometallic coordination frameworks, nevertheless we reckoned that the combination of the simple connector bipyMO with  $M(\text{hfac})_2$  and  $M'(\text{hfac})_2$  nodes could work, just for its simplicity. When an acetonitrile suspension of the copper and manganese compounds, **3** and **4**, in 1:1 molar ratio was refluxed, a solution quickly formed. By cooling to room temperature greenish crystals of the product **7** were obtained in high yield. The IR spectrum of **7**, although similar to the ones of **3** and **4**, does not appear to be the sum of the spectra of the two homometallic polymers (Figure S1). Moreover, SEM-EDS analyses carried out on a ground sample of **7** exploring several small areas of the sample to assess the relative metal content showed a constant unitary copper/manganese atomic ratio. Single crystal X-Ray diffraction studies established that the product was isotypic with the homometallic species **3-4** and was a coordination polymer where the two metal ions regularly alternated with *trans*- $\text{Cu}(\text{hfac})_2N_2$  and *trans*- $\text{Mn}(\text{hfac})_2O_2$  coordination environments. The molecular structure of a fragment of **7** is shown in Fig. 4.



**Figure 4.** Molecular structures of a fragment of the heterometallic CP **7**.

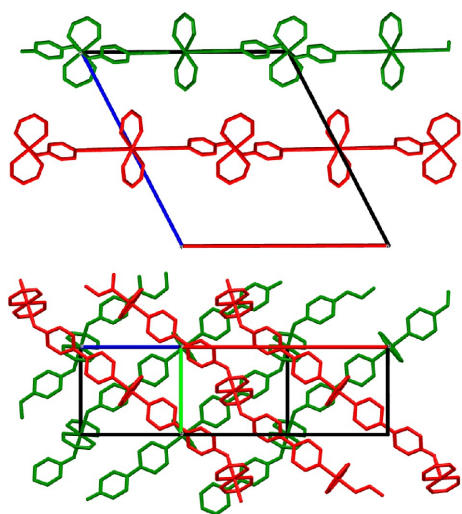
In order to test the reliability of the structural study in distinguishing the two metal atoms, which differ by only five electrons, at the end of the structure refinement we have interchanged the metal positions leaving the other atoms of the model at their place. After 10 refinement cycles the altered model converged to a minimum, but the *R* factor raised from 0.0448 to 0.0775 and a peak of +1.30  $e^-/\text{\AA}^3$  appeared on the difference Fourier map in correspondence of the new Mn position and a hole of  $-1.13 e^-/\text{\AA}^3$  appeared in correspondence of the new Cu position. On the basis of this result we believe reliable the attribution of the metal identity in the structure of **7**. In agreement with the larger atomic radius, the volumes of the Mn coordination octahedrons are greater than those of Cu and in the homometallic polymers the octahedrons  $\{\text{MO}_4\text{N}_2\}$  are slightly greater than the  $\{\text{MO}_6\}$  ones (Table 3). It can be noticed as a clue of the copper preference for nitrogen, that the difference in the volumes of these two octahedrons is smaller for copper than for manganese suggesting a stronger N–M bond for copper. In agreement with our attribution of the metal identity in the heterometallic polymer **7**, the coordination polyhedra  $\{\text{MnO}_6\}$  and  $\{\text{CuO}_4\text{N}_2\}$  show approximately the same volume they have in the homometallic derivatives. In addition, the bond distances attributed to Cu–N in **7** appear to be essentially identical to those in **3** and significantly different from the Mn–N bond distances in **4**, corroborating the characterization of **7** as an ordered heterometallic species. Moreover, a comparison with structural data of the homometallic copper(II) and manganese(II) coordination polymers having 2,5-bis(4-ethynylpyridyl)furan (bipyfu) as connector,  $[\text{M}(\text{hfac})_2(\text{bipyfu})]$ , [15] supports our assignment, reporting M–N bond distances 2.238(3) and 2.005(2) for M = Mn and Cu, respectively. Therefore, the selection of the nitrogen donor site by copper and of the oxygen donor site by manganese allows the formation of a species that appears to be the first example of a self-assembled heterometallic coordination polymer obtained using the simple divergent heterotopic bipyMO.

It is interesting to note that heterometallic CPs containing copper(II) and manganese(II) have received remarkable attention, the success of their preparation being related to the use of particular heterotopic ligands as *o*-phenylene-bis-oxamato, [16] 1,3-propylene-bis-oxamato, [17] macrocyclic oxamide, [18] N-phosphonomethyl(iminodiacetato) [19] or other dissymmetric compartmental ligands.[20]

**Table 3.** Comparison among coordination polyhedral of **3**, **4** and **7**.

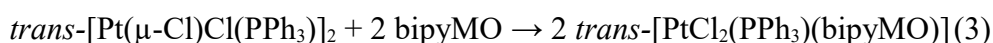
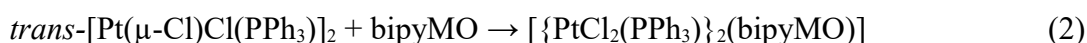
Compound	$\text{MO}_6$ octahedron				$\text{MO}_4\text{N}_2$ octahedron			
	M–O(1)	M–O(2)	M–O(3)	Volume ( $\text{\AA}^3$ )	M–N	M–O(4)	M–O(5)	Volume ( $\text{\AA}^3$ )
<b>3</b>	1.993(3)	2.010(3)	2.181(3)	11.63	2.026(3)	2.093(3)	2.122(3)	11.99
<b>4</b>	2.132(2)	2.149(2)	2.161(3)	13.15	2.272(3)	2.122(3)	2.151(3)	13.76
<b>7</b>	2.131(2)	2.136(2)	2.143(2)	12.96	2.022(3)	2.105(3)	2.107(3)	11.96

Fig. 5 shows the crystal structure common to the three polymers, **3**, **4** and **7**. Parallel chains running in the (1 2 0) direction makes layers perpendicular to the  $c^*$  direction. The chains belonging to a same layer are drawn by the same colour in Figure. The neighbouring layers have the chains directed in an almost perpendicular direction  $[1 \bar{2} 0]$ . This layout is common to **3**, **4** and **7**, but looking at Table 1 it appears that while **3** and **7** have approximately the same cell volume, **4** have a unit cell greater by among 3.5%. This is mainly due to a greater distance among the chains inside each layer as well to a less compact layer packing in the manganese CP.



**Figure 5.** Crystal structure of the chains  $\frac{1}{2}[\text{M}(\text{hfac})_2(\text{bipyMO})]$  projected along  $b$  (over) and along  $c^*$  (below).  $\text{CF}_3$  groups and hydrogens are omitted for clarity

Besides the reactions aimed to the synthesis of coordination polymers, we have also reacted bipyMO with a species able to offer only a single metal coordination site per metal centre. The treatment of the dinuclear chloro-bridged platinum(II) complex,  $\text{trans}-[\text{Pt}(\mu\text{-Cl})\text{Cl}(\text{PPh}_3)]_2$ , could in fact be expected to react with bipyMO with splitting of the chloro-bridges and formation of the di- or mono-nuclear complex in dependence of the metal to ligand molar ratio (Eqs 2 and 3).

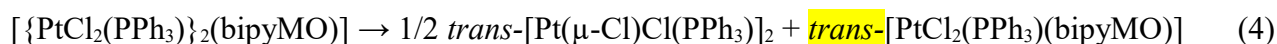


The dinuclear platinum complex is a useful precursor for the preparation of platinum(II) derivatives. [Errore: sorgente del riferimento non trovata] For instance, its reaction with 4,4'-bipyridyl (bipy) in 1:1 molar ratio produced the dinuclear  $\{[\text{PtCl}_2(\text{PPh}_3)]_2(\text{bipy})\}$ . [21] Moreover, when carried out in 1:2 molar ratio the reaction proceeded giving a mixture where  $\{[\text{PtCl}_2(\text{PPh}_3)]_2(\text{bipy})\}$ ,  $[\text{PtCl}_2(\text{PPh}_3)$

(bipy)] and free bipy were present in equilibrium and only by addition of a bipy excess [ $\{\text{PtCl}_2(\text{PPh}_3)\}_2(\text{bipy})$ ] was completely converted to  $[\text{PtCl}_2(\text{PPh}_3)(\text{bipy})]$  containing the hypodentate divergent ligand. [Errore: sorgente del riferimento non trovata] On the contrary, we observed that the reaction of *trans*- $[\text{Pt}(\mu\text{-Cl})\text{Cl}(\text{PPh}_3)]_2$  with bipyMO in 1:1 molar ratio, carried out in  $\text{CDCl}_3$  and monitored by  $^1\text{H}$  NMR spectroscopy evolved with the conversion of only a half of the platinum precursor to a product, reasonably the mononuclear *trans*- $[\text{PtCl}_2(\text{PPh}_3)(\text{N})\text{bipyMO}]$ .

The addition of a second equivalent of bipyMO brought to the complete disappearance of the poorly soluble orange *trans*- $[\text{Pt}(\mu\text{-Cl})\text{Cl}(\text{PPh}_3)]_2$  affording a yellow solution. NMR spectra showed the signals already observed at the previous step, that were definitely attributed to *trans*- $[\text{PtCl}_2(\text{PPh}_3)(\text{N})\text{bipyMO}]$ , as discussed below. The *trans*-isomer is indeed expected to be the kinetic product of the reaction, for the strong *trans*-effect exerted by  $\text{PPh}_3$  in the bridge splitting reaction, [Errore: sorgente del riferimento non trovata] as previously observed in the reaction of *trans*- $[\text{Pt}(\mu\text{-Cl})\text{Cl}(\text{PPh}_3)]_2$  with several N-donor ligands. [Errore: sorgente del riferimento non trovata] Moreover, this hypothesis is confirmed by the  $^{31}\text{P}$  spectrum where the signal at 2.6 ppm showing a phosphorous-platinum coupling constant of 3597 Hz is in agreement with this configuration (Table 4). The hypodentate bipyMO was supposed to be N-coordinated to platinum, not only in consideration of the higher platinum affinity towards N- rather than O-donor ligands, but also for the chemical shift of the NCH protons, similar to the corresponding protons in the pyridine (py) derivative [*trans*- $[\text{PtCl}_2(\text{PPh}_3)(\text{py})]$ ] [Errore: sorgente del riferimento non trovata] (9.03 ppm) and significantly different from the NCH protons of [*cis*- $[\text{PtCl}_2(\text{PPh}_3)(\text{py})]$ ] at 8.45 ppm (Table 4). The complete assignment of the signals in  $^1\text{H}$ -,  $^{13}\text{C}$ -,  $^{31}\text{P}$  and  $^{195}\text{Pt}$ -NMR spectra of *trans*-**8** is reported in SI.

It is worth to note that the outcome of the reaction between *trans*- $[\text{Pt}(\mu\text{-Cl})\text{Cl}(\text{PPh}_3)]_2$  and bipyMO in 1:1 molar ratio suggests that [ $\{\text{PtCl}_2(\text{PPh}_3)\}_2(\text{bipyMO})$ ] is unstable with respect to *trans*- ( $[\text{Pt}(\mu\text{-Cl})\text{Cl}(\text{PPh}_3)]_2 + \text{trans-}[\text{PtCl}_2(\text{PPh}_3)(\text{bipyMO})]$ ) (Eq 4).

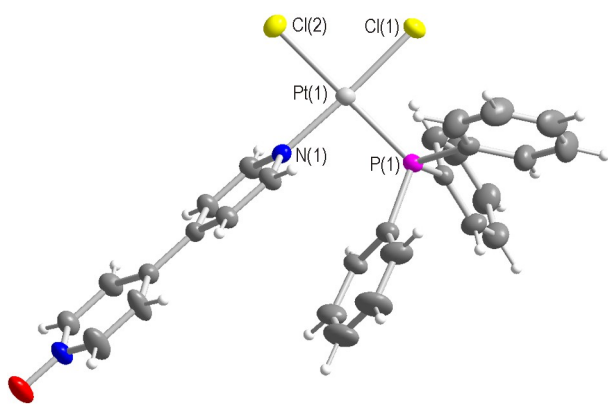


Therefore, in the presence of the potential [N],[O]-donor connector bipyMO, the metal centre preferences direct the reaction towards the formation of the mononuclear complex containing the hypodentate N-bonded ligands and maintaining about half chloro-bridged complex, contrary to what happens with other divergent N,N-donor ligands. [Errore: sorgente del riferimento non trovata] In other words, the comparison between the two systems *trans*- $[\text{Pt}(\mu\text{-Cl})\text{Cl}(\text{PPh}_3)]_2/\text{bipy}$  and *trans*- $[\text{Pt}(\mu\text{-Cl})\text{Cl}(\text{PPh}_3)]_2/\text{bipyMO}$  evidences that the chloride bridge splitting is favoured when

a N-donor ligand enters the metal coordination sphere while does not proceed if an O-donor ligand is available.

Although yellow  $\text{CHCl}_3$  solutions of *trans*- $[\text{PtCl}_2(\text{PPh}_3)(\text{bipyMO})]$  could be stored for several hours without any evident change, the addition of a small amount of free ligand produced the progressive fading of the solution due to isomerization with consequent precipitation of a little soluble colourless product. The formation of *cis*- $[\text{PtCl}_2(\text{PPh}_3)(\text{bipyMO})]$ , *cis*-**8**, can be rationalized on the base of the well known free ligand catalyzed isomerisation of platinum(II) complexes. [22] This hypothesis was corroborated by NMR spectroscopy and confirmed by single crystal X-ray diffraction measurements. Because of the poor solubility of *cis*-**8** in chloroform,  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectra were carried out in  $\text{CD}_3\text{CN}$ . The signal at 6.4 ppm with phosphorous-platinum coupling constant of 3881 Hz in the  $^{31}\text{P}$  NMR spectrum and the signal at 8.49 ppm assigned to the NCH protons in the  $^1\text{H}$  NMR were in agreement with the *cis*-geometry of the species (Table 4). The complete assignment of the signals ( $^1\text{H}$ - and  $^{31}\text{P}$ -NMR spectra) is reported in SI.

The molecular structure of **8** is shown in Fig. 6. The Pt atom is co-ordinated by two Cl, one phosphorus and one nitrogen atom in an approximately square planar geometry. The square distortion is mainly due to the difference in bond lengths of the different ligands. Pt–N distance is exactly the same of that found in the other example of  $\text{Pt}^{\text{II}}$ –bipyMO compound. [Errore: sorgente del riferimento non trovata] The Pt–Cl(2) distance is markedly longer than that from Cl(1) due to the *trans* effect of the phosphine. In the solid state the uncoordinated -NO group is involved in a hydrogen bond with the crystallization solvent  $\text{CDCl}_3$ .



**Figure 6.** Molecular structure of *cis* $[\text{PtCl}_2(\text{PPh}_3)(\text{bipyMO})]$ . Bond distances ( $\text{\AA}$ ) around Pt atom: Pt(1)–Cl(1) 2.3020(17), Pt(1)–Cl(2) 2.3593(17), Pt(1)–P(1) 2.2395(17), Pt(1)–N(1) 2.035(5).

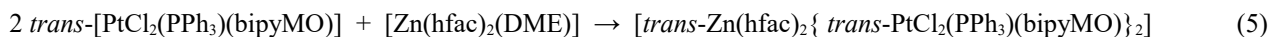


Our results suggested that the soluble *trans*-[PtCl<sub>2</sub>(PPh<sub>3</sub>)(bipyMO)], having pendant oxygen donor functionalities and being inert to isomerization in the absence of free ligand, was in principle able to make further bonds towards more oxophilic centres and therefore was a good precursor for the preparation of heterometallic compounds in mild conditions.

Table 4- Comparison of NMR significant signals (CDCl<sub>3</sub>, \*CD<sub>3</sub>CN) of **8** and **9**

complex	$\delta$ NCH ppm	$\delta$ ONCH ppm	$\delta$ P/ppm ( <sup>1</sup> J <sub>P-Pt</sub> /Hz)
<i>trans</i> - <b>8</b>	9.13	8.36	2.64 (3603)
<i>cis</i> - <b>8</b>	8.49	8.20	6.34 (3887)
<b>9</b> *	9.20	8.56	2.62 (3620)
<i>trans</i> -PtCl <sub>2</sub> (PPh <sub>3</sub> )(py) Errore: sorgente del riferimento non trovata	9.03	---	2.59 (3581)
<i>cis</i> -PtCl <sub>2</sub> (PPh <sub>3</sub> )(py) Errore: sorgente del riferimento non trovata	8.45	---	7.24 (3904)
Py	8.74	---	---
bipyMO	8.77	8.33	---

*trans*-**8** was then reacted with [Zn(hfac)<sub>2</sub>(DME)], **1**, in 2:1 molar ratio affording the tri-nuclear derivative *trans*-[Zn(hfac)<sub>2</sub>{*trans*-PtCl<sub>2</sub>(PPh<sub>3</sub>)(bipyMO)}<sub>2</sub>], **9** (Eq 5).



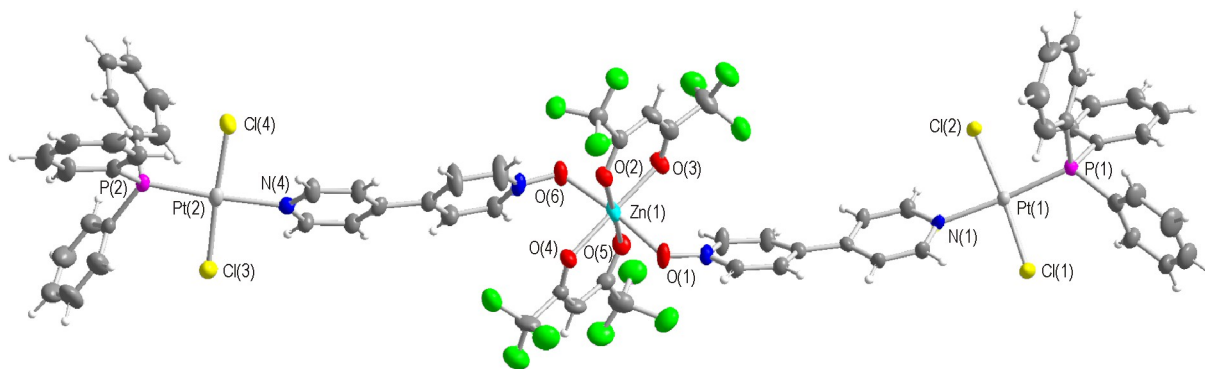
The NMR spectra were in excellent agreement with this formulation showing the diagnostic resonances of the NCH (<sup>1</sup>H: 9.20 ppm) and of the PPh<sub>3</sub> (<sup>31</sup>P: 2.62 ppm; <sup>1</sup>J<sub>P-Pt</sub> 3620 Hz). (Table 4). The complete assignment of the signals in <sup>1</sup>H-, <sup>13</sup>C-, <sup>31</sup>P-, <sup>195</sup>Pt- and <sup>19</sup>F-NMR spectra of **9** is reported in SI.

The product was crystallized by slow diffusion of pentane in a toluene solution. X-ray diffraction measurements showed the product was a trinuclear complex formed by a central zinc ion *trans*-O-coordinated to two *trans*-[PtCl<sub>2</sub>(PPh<sub>3</sub>)(bipyMO)] metallo ligands in an approximately octahedral environment.

The molecular structure of *trans*-[Zn(hfac)<sub>2</sub>{*trans*-PtCl<sub>2</sub>(PPh<sub>3</sub>)(bipyMO)}<sub>2</sub>] is shown in Fig. 7. Selected bond distances are listed in the caption. Coordination around Pt is similar to that found in *cis*-**8**, but the *trans* configuration makes the Pt–Cl distances very close to each other. The *trans* influence of the phosphine affects in this case the Pt–N bonds which becomes slightly longer, from 2.03 to about 2.11 Å. The Zn centre is octahedrally coordinated like it is in the structure of **1**, but also in this case the *trans* disposition of the bipyMO ligands slightly modifies the geometry. The Zn–O<sub>hfac</sub> distances slightly raise, while Zn–O<sub>bipyMO</sub> ones are shorter than those of Zn–O<sub>DME</sub>. The



volume of Zn coordination octahedron, however, is slightly greater in **9**, 12,03 Å<sup>3</sup>, than in **1**, 11,84 Å<sup>3</sup>.



**Figure 7.** Molecular structure of *trans*[Zn(hfac)<sub>2</sub>{*trans*-PtCl<sub>2</sub>(PPh<sub>3</sub>)(bipyMO)}<sub>2</sub>], **9**. Bond distances (Å) around Pt atom: Pt(1)–Cl(1) 2.273(3), Pt(1)–Cl(2) 2.285(3), Pt(1)–P(1) 2.238(3), Pt(1)–N(1) 2.097(8), Zn(1)–O(1) 2.150(9), Zn(1)–O(2) 2.061(8), Zn(1)–O(3) 2.063(8), Zn(1)–O(4) 2.064(8), Zn(1)–O(5) 2.052(8), Zn(1)–O(6) 2.114(9), Pt(2)–Cl(3) 2.265(3), Pt(2)–Cl(4) 2.289(3), Pt(2)–P(2) 2.232(3), Pt(2)–N(4) 2.121(9).

## 4. Conclusions

In this work two different approaches have been faced to prepare self-assembled heterometallic compounds exploiting the selection potentialities of the divergent heterotopic ligand bipyMO. The former approach originated from the synthesis and characterization of the isotypical mono-dimensional CPs  $\infty$ [M(hfac)<sub>2</sub>(bipyMO)] (M = Zn, Cu, Co, Mn). They were found to contain two different approximately octahedral metal sites *trans*-M(hfac)<sub>2</sub>[N]<sub>2</sub> and *trans*-M(hfac)<sub>2</sub>[O]<sub>2</sub>, one completing its coordination sphere with two nitrogen- and the other with two oxygen-coordinated bipyMO. Therefore, in presence of two different metal sites, a self-assembling process could be directed by the different affinity of nitrogen and oxygen towards the two different metal ions leading to a regular alternated sequence of the two metal ions in a mono-dimensional heterometallic CP. Indeed, the reaction between the two copper and manganese homo-metallic CPs led to the formation of the heterometallic species  $\infty$ [Cu(hfac)<sub>2</sub>Mn(hfac)<sub>2</sub>(bipyMO)<sub>2</sub>] containing the ordered sequences Cu(hfac)<sub>2</sub>[N]<sub>2</sub>–Mn(hfac)<sub>2</sub>[O]<sub>2</sub>.

The second approach derived from the outcome of the reaction of bipyMO with the platinum(II) complex *trans*-[PtCl(μ-Cl)(PPh<sub>3</sub>)<sub>2</sub>], able to generate a free coordination site on each metal centre by the chloro-bridge splitting. The reaction, also when carried out with a Pt:ligand molar ratio 2:1, yielded the mononuclear species *trans*-**8** containing the hypodentate N-coordinated ligand, instead of the expected dinuclear species containing the Pt–N—NO–Pt core, at variance with what previously observed with the divergent homotopic ligand 4,4'-bipyridine that produced, as a single product, the dinuclear species having the central Pt–N—N–Pt moiety (–N—NO– and –N—N– representing the bridging bipyMO and bipy, respectively). With bipyMO the preference of the metal for the nitrogen atom is so marked to leave the oxygen atom not bonded but only engaged in a

hydrogen bond interaction with the solvent ( $\text{CHCl}_3$ ), as revealed by the solid state structural characterization, while half precursor remains unreacted. The pendant donor functionality can provide a further bond with metal centres having a binding site available in their coordination sphere. Such a “complex as ligand strategy” was applied with success to the synthesis of the heterometallic compound *trans*- $[\text{Zn}(\text{hfac})_2\{\text{trans-PtCl}_2(\text{PPh}_3)(\text{bipyMO})\}_2]$ .

In summary, we report in this paper the facile synthesis and the crystallographic characterization of the first heterometallic coordination polymer and of the first hetero-metallic molecular complex showing bipyMO as bridging ligand between two different metals. Families of self-assembled hetero-bimetallic derivatives (containing for instance early-late transition metals or 3*d*-4*f* metals) appear potentially at hand based on the selection power exerted by bipyMO: these studies are ongoing in our labs, taking also into account the peculiar properties (magnetic, optic, catalytic) of the designed hetero-metallic products.

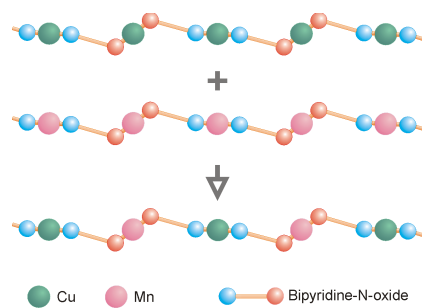
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## Appendix A, Supplementary Data

CCDC 1560242-47 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif), or by emailing [data\\_request@ccdc.cam.ac.uk](mailto:data_request@ccdc.cam.ac.uk), or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033. Supporting information (SI) available: NMR data of *trans*-8, *cis*-8 and 9, ATR-FTIR spectra of 3, 4 and 7.

## Table of Content Graphics



The simple heterotopic divergent ligand N-oxide-4,4'-bipyridine has been used in a self assembling process to prepare a regularly alternated heterobimetallic 1D coordination polymer or as a bidentate ligand in a “complex as ligand strategy” to prepare heterobimetallic compounds.

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