

Synthesis and Characterization of Acyclic and Cyclic Aza-bridged Ligands Incorporating 2,2'-Bipyridine Subunits and Their Complexes With Copper(II), Cobalt(II), and Nickel(II)

Antonino Mamo* and Andrea Pappalardo

Department of Physical and Chemical Methodologies for Engineering, Engineering Faculty, University of Catania, V.le Andrea Doria 6, I-95125 Catania, Italy. Tel. (+39) 95-7382756, Fax (+39) 95-333231.

* Author to whom correspondence should be addressed; e-mail: mamo@dmfci.ing.unict.it

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Abstract: The synthesis of a series of *N,N'*-disubstituted acyclic (**AL**) and cyclic (**CL**) aza-bridged ligands incorporating 2,2'-bipyridine subunits is described. ¹H-NMR and IR spectral data support the proposed ligand structures. Dynamic ¹H-NMR studies on diurea and diamide derivatives point to the presence of slowly interconverting conformers on the ¹H-NMR time-scale, owing to N–H···N hydrogen bonding and/or a restricted rotation around the amide bonds. The ligands synthesized form 1:1 complexes with divalent transition metal ions. Upon complexation, bis-ester derivatives **AL**₅ and **CL**₅ undergo a metal-induced hydrolysis of the ester groups to carboxyl functions, which act as additional binding sites for the metal ion, as well as hydrogen-bonding donor-acceptor binding site to produce dimeric complexes.

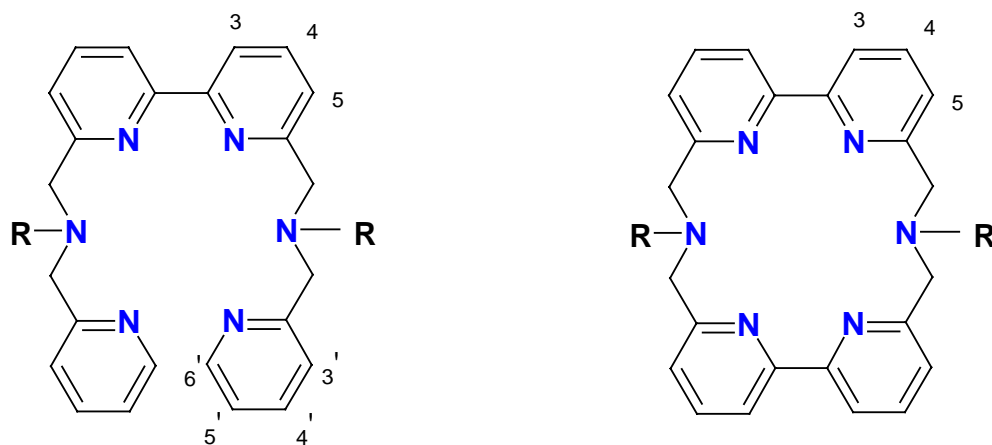
Keywords: Transition metal complexes; bipyridine derivatives; polydentate aza-ligands; macrocycles; dynamic NMR

Introduction

Although 2,2'-bipyridine has been used as a classic bidentate ligand for over a century, only in the last two decades has this subunit been widely employed in the design of photoactive cryptands [1], polyfunctionalized ligands [2], dendrimers and star-like macromolecules [3]. In view of the potential offered by polymer-bound bipyridines and their transition-metal complexes in analytical chemistry [4] and in photochemical processes [5], we became interested in the synthesis of a variety of rigid and flexible polyamides and polyurethanes incorporating acyclic (**AL**₁, Acyclic Ligand) and cyclic (**CL**₁, Cyclic Ligand) bipyridinediyl diamino subunits (complexing building blocks) within the polymeric backbone [6,7]. These materials were shown to form polynuclear complexes with the first-row transition metals [6].

Current interest in macromolecular complexes bearing bipyridine chelating units [8] prompted us to design a number of acyclic and cyclic polypyridine ligands, to be exploited as model ligands for a better understanding of the coordination properties of related macromolecular systems. In this paper we wish to report the synthesis, structural characterization and fluxional properties of the ligands **AL**₂₋₅ and **CL**₂₋₅ shown in Scheme 1, as well as the preparation and characterization of their complexes with divalent transition metals Cu(II), Co(II), and Ni(II).

Scheme 1



Ligand	R	Ligand	R
AL ₁	H	CL ₁	H
AL ₂	COCH ₃	CL ₂	COCH ₃
AL ₃	COPh	CL ₃	COPh
AL ₄	CONHPh	CL ₄	CONHPh
AL ₅	CH ₂ CO ₂ Bu ^t	CL ₅	CH ₂ CO ₂ Bu ^t
AL ₆	CH ₂ COOH	CL ₆	CH ₂ COOH

Results and Discussion

Ligands **AL**_{1,3} and **CL**_{1,3} were synthesized by literature procedures [2,6,9]. *N,N'*-Diacetyl and bis-urea derivatives **AL**₂, **CL**₂ and **AL**₄, **CL**₄ were prepared by reaction of the appropriate acyclic or cyclic bis-amine with Ac₂O/Et₃N or phenyl isocyanate, respectively, in anhydrous CHCl₃ at room temperature (r.t.). Bis-esters **AL**₅ and **CL**₅ were produced in good yield by *N*-alkylation of the parent diamines with *t*-butyl bromoacetate/K₂CO₃ in dry CH₃CN. The structural characterization of all new compounds was accomplished by elemental analysis, FAB (+) MS measurements, and ¹H-NMR spectroscopy. The ¹H-NMR spectral data for acyclic and cyclic ligands are reported in Tables I and II, respectively.

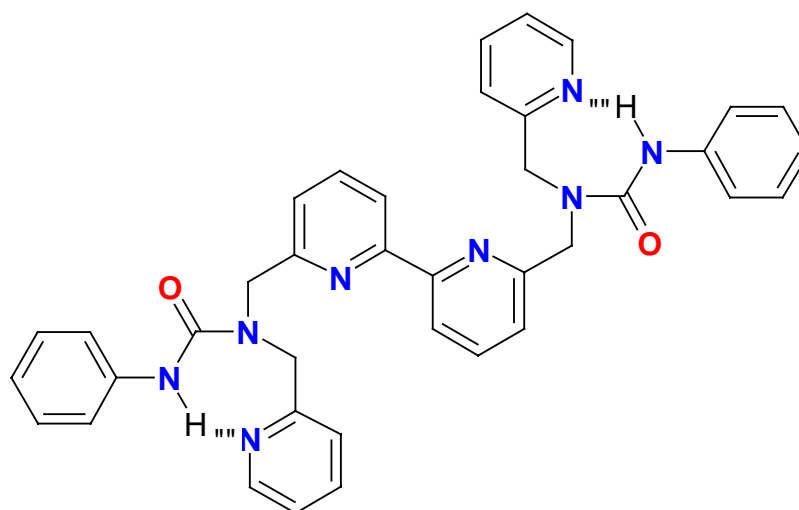
Table I. ¹H-NMR parameters of acyclic ligands **AL**₂ – **AL**₅.

Proton	AL ₂ 293 K	AL ₃ 293 K	AL ₃ 373 K	AL ₄ 293 K	AL ₅ 293 K
3	8.29 – 8.21 m	8.34 – 8.24 m	8.45 d <i>J</i> = 7.8	8.23 d <i>J</i> = 7.7	8.29 dd <i>J</i> = 7.7; 0.9
4	7.80 – 7.59 m	7.82 – 7.77 m	7.78 t <i>J</i> = 7.8	7.72 t <i>J</i> = 7.7	7.77 t <i>J</i> = 7.7
5	7.29 – 7.12 m	7.09 d <i>J</i> = 7.4	7.24 d <i>J</i> = 7.8	7.46 d <i>J</i> = 7.9	7.55 dd <i>J</i> = 7.7; 0.9
α + γ CH₂	4.78, 4.71 s	4.92 d <i>J</i> = 4.7 4.76, 4.71 s	4.91, 4.85 s	4.75, 4.70 s	4.04 s
3'	7.29 – 7.12 m	7.53 bd <i>J</i> = 7.5	7.31 d <i>J</i> = 8.1	7.46 d <i>J</i> = 7.9	7.67 – 7.65 m
4'	7.80 – 7.59 m	7.72 – 7.65 m	7.65 t <i>J</i> = 8.1	7.60 dt <i>J</i> = 7.7; 1.7	7.67 – 7.65 m
5'	7.29 – 7.12 m	7.22 – 7.18 m	7.18 – 7.13 m	7.18 m	7.18 – 7.14 m
6'	8.57, 8.49 dd <i>J</i> = 4.1–4.7; 0.8	8.57, 8.53 d <i>J</i> = 4.5; 0.9	8.58 d <i>J</i> = 4.8	8.59 d <i>J</i> = 4.3	8.54 dt <i>J</i> = 4.7; 1.3
CH₂	–	–	–	–	3.40 s
CH₃	2.28, 2.21 s	–	–	–	1.47 s
NH	–	–	–	9.97 bs	–
Ph	–	7.60 – 7.31 m	7.59 – 7.34 m	7.03 t <i>J</i> = 7.4 7.32 – 7.17 m	–

Notes: The spectra were obtained in deuterated tetrachloroethane (TCE). Chemical shifts are reported in ppm, and coupling constants (*J*) in Hz. Numbering pattern as shown in Scheme 1. Abbreviations used: bs = broad singlet, s = singlet, d = doublet, dd = double doublet, m = multiplet, t = triplet, dt = double triplet.

The $^1\text{H-NMR}$ spectra of acyclic bis-amide ligands $\text{AL}_{2,3}$ (not shown) are quite complex, and can be interpreted in terms of two overlapping sets of signals, arising from a mixture of rotamers in slow equilibrium on the $^1\text{H-NMR}$ time-scale, due to the restricted rotation around the amide bonds. In both compounds the ratio between the two rotamers at 293 K in chlorinated solvents is about 3:2, as it can be deduced by integration of the pair of methyl singlets in AL_2 and of the pair of H^6 doublets in AL_3 . Dynamic NMR studies on AL_3 have shown that, upon heating a TCE solution of the ligand, broadening of most signals occurred, with a coalescence temperature at about 340 K, followed by sharpening at more elevated temperatures, corresponding to the free rotation of the benzoyl groups. Well resolved spectra were obtained at temperatures as high as 373 K, showing the characteristic three-spin system for the bipyridyl unit, and four-spin system for a 2-substituted pyridyl ring. From the dynamic parameters a $\Delta G = 17.2$ Kcal/mol was ascertained for the torsional energy of the amide bond.

Scheme 2



In spite of the presence of two ureido moieties, the r.t. $^1\text{H-NMR}$ spectrum of acyclic diurea AL_4 in TCE displays sharp resonances for both aromatic and methylene protons, due to the locking of rotamers by the formation of intramolecular hydrogen bonding between the N-H proton and the juxtaposed pyridine ring nitrogen (Scheme 2), as suggested by the broad downfield resonance of the N-H groups at δ 9.97 ppm. As expected, *N*-alkylated diester AL_5 is a flexible molecule and, due to partial overlapping of the heteroaromatic protons, decoupling experiments were used for proton assignments. Noteworthy, the H^3 bipyridyl protons of $\text{AL}_{2,5}$ resonate in the range 8.45–8.25 ppm, a region considered of diagnostic value for an *anti* orientation of the bipyridyl unit [10].

Table II. $^1\text{H-NMR}$ parameters of cyclic ligands $\text{CL}_2 - \text{CL}_5$

Proton	CL_2 293 K	CL_2 403 K	CL_3 403 K	CL_4 403 K	CL_5 293 K
3	7.72, 7.70, 7.64, 7.57 dd $J = 7.4 - 7.7; 0.8$	7.63 d $J = 7.7$	7.65 dd $J = 7.8; 0.9$	7.65 d $J = 7.5$	7.68 d $J = 7.7$
4	7.42, 7.37, 7.31, 7.20 t $J = 7.7$	7.34 bt	7.39 t $J = 7.7$	7.36 t $J = 7.5$	7.29 t $J = 7.7$
5	7.21, 6.98, 6.64, 6.52 dd $J = 7.4 - 7.7; 0.8$	6.90 hump	7.13 bd $J = 7.6$	6.85 d $J = 7.5$	7.12 d $J = 7.7$
α - + γ - CH_2	4.87, 4.90 s 4.96 bs	4.91 s	4.96 s	4.89 bs	4.08 s
CH₂	–	–	–	–	3.73 s
CH₃	2.42, 2.44 s	2.41 s	–	–	1.56 s
NH	–	–	–	9.48 bs	–
Ph	–	–	7.81 – 7.78; 7.47 – 7.44 m	7.53 d $J = 9.0$; 7.18, 7.10 t $J = 6.8$	–

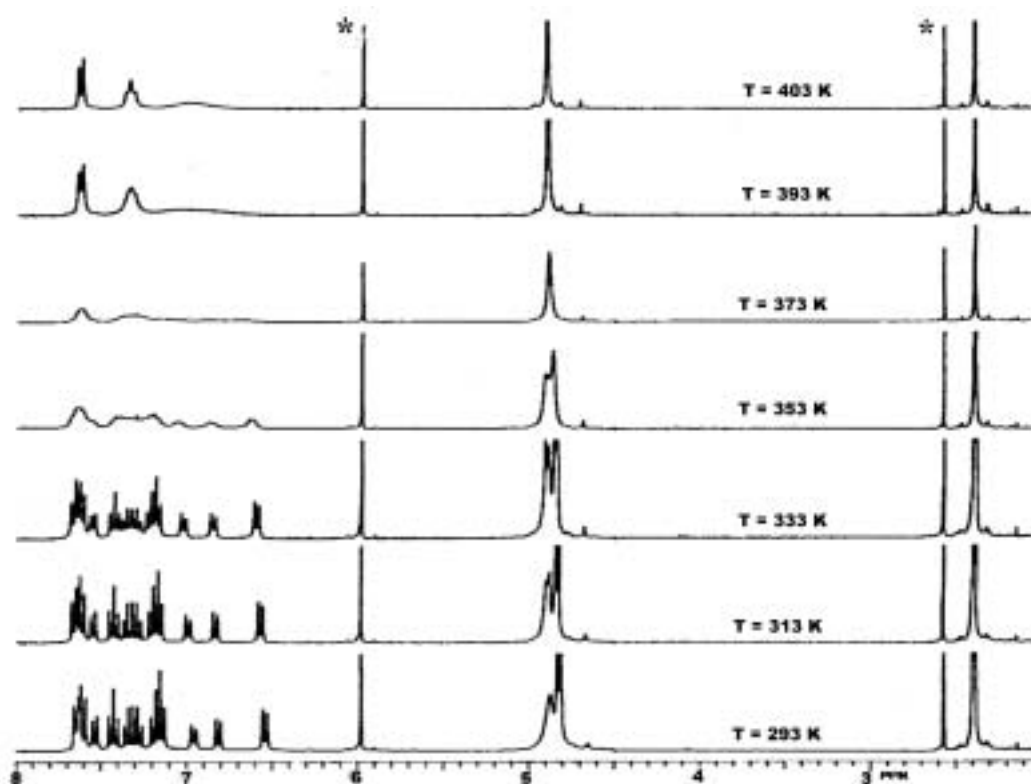
Notes: The spectra were obtained in deuterated TCE. Chemical shifts are reported in ppm, and coupling constants (J) in Hz. Numbering pattern as shown in Scheme 1. Abbreviations used: bs = broad singlet, s = singlet, d = doublet, dd = double doublet, m = multiplet, t = triplet, dt = double triplet.

The 293 K $^1\text{H-NMR}$ spectrum (CDCl_3) of CL_2 (Figure 1) shows two singlets for the methyl groups, one broad and two sharp singlets for the bridging methylenes, and two sets of well-resolved resonances for the bipyridyl protons, spread out in the 6.5–7.7 ppm region. These spectral data may be suggestive of the presence of two slowly interconverting diastereomeric forms of CL_2 (in a ratio of ca. 3:2). Each of the two conformers features two pairs of pyridyl subunits in different magnetic environments, resulting in a total of four double doublets for H^3 and H^5 protons, and four triplets for H^4 protons (Table II and Figure 1).

Interconversion between the two forms may be realized by rotation of the acetyl group(s) around the amide bond(s). In order to measure the energy barrier associated with this process, a VT NMR study of CL_2 was undertaken, using deuterated TCE as a solvent, with the results shown in Figure 1. On raising the temperature, broadening of the signals was observed above 340 K, and coalescence occurred at about 373 K. At 403 K the signals of methylene and H^3 protons show up as a sharp singlet and a doublet, respectively, while H^4 protons appear as a broad triplet and H^5 protons are still broad.

Higher temperatures were precluded by the solvent used. From the dynamic parameters a $\Delta G = 19.0$ kcal/mol was ascertained for conformational transitions.

Figure 1. Variable Temperature (VT) $^1\text{H-NMR}$ spectra of CL_2 in TCE.



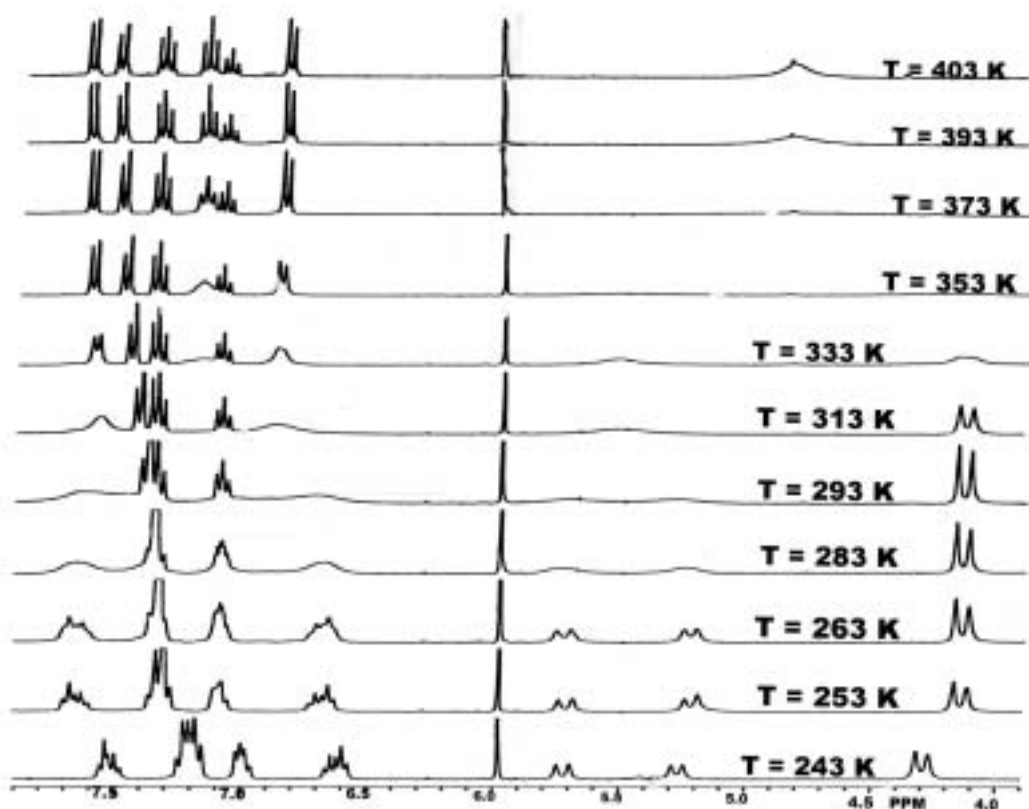
* Residual solvent peaks

The room temperature $^1\text{H-NMR}$ spectrum of CL_3 is very broad in every region, again suggesting the presence of at least two conformers slowly interconverting on the $^1\text{H-NMR}$ scale. The methylene protons show up as two humps, which upon heating coalesce to a singlet at temperatures above 333 K, with simultaneous sharpening of the signals in the aromatic region. At 403 K (Table II) average signals are obtained, and the spectrum consists of a singlet at δ 4.96 ppm for the α and γ bridging methylenes, a broad doublet at δ 7.13 ppm for H^5 , a triplet at δ 7.39 for H^4 , a double doublet at δ 7.65 for H^3 , and two complex multiplets in a 3:2 ratio for the benzoyl protons, centered at δ 7.46 and 7.80 ppm, respectively. Unfortunately, the sparing solubility of the compound did not allow us to explore its behaviour at low temperatures.

The $^1\text{H-NMR}$ spectra of cyclic diurea CL_4 are also temperature dependent, and the results of its dynamic behaviour are shown in Figure 2. At 253 K the methylene protons show a pattern of three doublets at δ 4.12, 5.21 and 5.74 ppm (ratio 2:1:1), while the aromatic protons are ill-defined, owing to a considerable overlapping. Upon raising the temperature, the two downfield methylene doublets broaden and coalesce at about 313 K, with contemporary sharpening of a set of aromatic protons (assignable to the two phenyl groups) and broadening of the remaining bipyridyl protons (multiplets

centered at δ 6.62 and 7.6 ppm in the low temperature spectrum). At higher temperatures further broadening of the upfield methylene doublet and, concomitantly, of bipyridyl protons is observed. The two methylene humps coalesce to a broad singlet at temperatures above 373 K, and at 403 K the proton spectrum appears averaged by a fast motion of the molecule giving the complete equivalence of pertinent aromatic and methylene protons.

Figure 2. Variable Temperature (VT) $^1\text{H-NMR}$ spectra of CL_4 in TCE



The VT $^1\text{H-NMR}$ studies of CL_4 showed therefore two coalescence temperatures at 313 and 373 K, corresponding to conformational transitions with free energy barriers of 11.9 and 13.5 Kcal/mol, respectively. The first transition is likely associated with the breaking of intramolecular N-H \cdots N hydrogen bondings, while the second one is related to the torsional barrier around PhNHC(O)–N bonds.

Owing to the low solubility of AL_3 and CL_3 , the very similar AL_2 and CL_2 ligands were synthesized only in order to better understand the influence of the amido moiety on the conformational aspects.

As a general feature, the IR spectra of all acyclic or cyclic ligands show a 1600–1395 cm^{-1} region dominated by strong or medium-strong absorption bands associated with the stretching vibrational modes of heterocyclic rings [10, 11]. In addition, bis-amide ligands $\text{AL}_{2,3}$ and $\text{CL}_{2,3}$ display prominent carbonyl bands at 1650–1630 cm^{-1} , a frequency considered of diagnostic value for tertiary amides [12], while bis-urea derivatives AL_4 and CL_4 exhibit N-H stretching bands at 3280–3320 cm^{-1} , a carbonyl

absorption band, known as the Amide I band [6], at 1640-1670 cm^{-1} , and a N-H band, known as Amide II band [6], at 1525-1540 cm^{-1} . On the other hand, bis-ester ligands **AL₅** and **CL₅** show a C=O stretching band at 1740-1700 cm^{-1} along with CC(=O)-O stretching vibration and O-C-C asymmetric stretching bands at 1270 and 1163 cm^{-1} , respectively. Well resolved absorption bands are also present at lower frequencies, which can be ascribed to the in-plane and out-of-plane ring deformations [11,12].

The Cu(II), Co(II), and Ni(II) complexes with the new acyclic and cyclic ligands were prepared by reacting each ligand with the appropriate metal nitrate salt (1 equiv) in aqueous MeOH at room temperature. It is noteworthy that the synthesis of complex **CL_{4a}** was carried out at reflux. Table III shows the physicochemical characteristics of the synthesized complexes. Complexes **AL_{3a-c}** and **CL_{3a}** were prepared according to literature data [5] (the lettering **a**, **b**, and **c** refers to Cu(II), Co(II), and Ni(II) complexes, respectively).

Table III. Analytical and TGA data for the Complexes

Complex	Yield (%)	Analytical data				TGA
		Found (calculated)				
		Metal ^b	%C	%H	%N	
[Cu(AL ₃)(H ₂ O) ₂](NO ₃) ₂ ·2H ₂ O ^a AL_{3a}	75 CH ₃ CN	7.50 (7.35)	53.13 (52.80)	4.69 (4.66)	13.04 (12.96)	-2H ₂ O (50 °C); -2H ₂ O (100 °C); 210°C dec.
[Co(AL ₃)(H ₂ O) ₂](NO ₃) ₂ ·1H ₂ O ^a AL_{3b}	88 CH ₃ CN	6.83 (7.00)	53.82 (54.22)	4.39 (4.55)	13.56 (13.31)	-1H ₂ O (50 °C); -2H ₂ O (100 °C); 228°C dec.
[Ni(AL ₃)(H ₂ O) ₂](NO ₃) ₂ ·2H ₂ O ^a AL_{3c}	85 CH ₃ CN	6.43 (6.83)	52.83 (53.09)	4.06 (4.69)	12.74 (13.03)	-2H ₂ O(48°C); -2H ₂ O (110°C); 210°C dec.
[Cu(AL ₄)](NO ₃) ₂ AL_{4a}	68 MeOH/Et ₂ O	7.50 7.73	55.17 (55.50)	4.03 (4.17)	17.17 (17.03)	205 °C dec
[Co(AL ₄)](NO ₃) ₂ ·1CH ₃ CN AL_{4b}	64 CH ₃ CN	7.00 (6.86)	55.91 (55.94)	4.57 (4.34)	17.85 (17.94)	-1CH ₃ CN (40°C); 223°C dec.
[Ni(AL ₄)](NO ₃) ₂ ·1H ₂ O AL_{4c}	70 CH ₃ CN	6.77 (7.02)	55.01 (54.62)	3.90 (4.34)	17.01 (16.76)	-1H ₂ O(50°C); 227°C dec.
[Cu(AL ₅)](NO ₃) ₂ ·1H ₂ O AL_{5a}	52 CH ₂ Cl ₂ /C ₆ H ₁₂	7.10 (7.65)	51.72 (52.06)	5.49 (5.58)	13.74 (13.49)	-1H ₂ O(40°C);° 170°C dec.
[Co(AL ₅)](NO ₃) ₂ ·1H ₂ O AL_{5b}	48 CH ₂ Cl ₂ /C ₆ H ₁₂	7.01 (7.14)	51.98 (52.36)	5.15 (5.61)	13.92 (13.57)	-1H ₂ O(44°C); 200°C dec.
[Ni(AL ₅)](NO ₃) ₂ ·1H ₂ O AL_{5c}	43 CH ₂ Cl ₂ /C ₆ H ₁₂	7.23 (7.11)	52.13 (52.37)	5.67 (5.62)	13.60 (13.57)	-1H ₂ O(48°C); 180°C dec.

Table III. (cont.)

[Cu ₂ (AL ₆) ₂ H](NO ₃) ₃ ·4H ₂ O AL_{6a}	37 CH ₃ CN	9.17 (9.01)	47.98 (47.72)	4.83 (4.51)	15.25 (14.91)	-4H ₂ O (40 °C); 170°C, 235°C dec
[Co ₂ (AL ₆) ₂ H](NO ₃) ₃ ·4H ₂ O AL_{6b}	33 CH ₃ CN	8.13 (8.41)	47.93 (48.03)	4.65 (4.53)	15.32 (15.00)	-4H ₂ O (50 °C); 160°C; 270°C dec
[Ni ₂ (AL ₆) ₂ H](NO ₃) ₃ ·6H ₂ O AL_{6c}	38 CH ₃ CN	8.00 (8.17)	46.35 (46.84)	4.97 (4.70)	14.75 (14.63)	-6H ₂ O (50 °C); 108°C; 260°C dec
[Cu(CL ₃)](NO ₃) ₂ ·4H ₂ O ^a CL_{3a}	90 MeOH	7.49 (7.57)	52.89 (52.92)	4.10 (4.44)	13.04 (13.00)	-4H ₂ O (50 °C); 370 °C dec.
[Cu(CL ₄)](NO ₃) ₂ CL_{4a}	80 MeOH	7.72 (7.51)	55.67 (55.64)	3.86 (3.93)	17.25 (17.08)	325 °C dec.
[Cu ₂ (CL ₆) ₂ H](NO ₃) ₃ ·10H ₂ O CL_{6a}	70 MeOH/Et ₂ O	8.39 (8.44)	44.83 (44.44)	4.48 (4.72)	13.51 (13.88)	-10H ₂ O (40 °C); 180°C; 385°C dec
[Co ₂ (CL ₆) ₂ H](NO ₃) ₃ ·7H ₂ O CL_{6b}	75 CH ₃ CN	8.12 (8.01)	45.94 (46.38)	4.07 (4.51)	14.78 (14.49)	-7H ₂ O (50 °C); 168°C; 370°C dec
[Ni ₂ (CL ₆) ₂ H](NO ₃) ₃ ·7H ₂ O CL_{6c}	82 MeOH	8.09 (7.93)	46.36 (46.38)	4.11 (4.51)	14.29 (14.49)	-7H ₂ O (50 °C); 145°C; 365°C dec

^a From Ref. [6]; ^b Determined by AA

The acyclic ligands **AL₃₋₅** generally give stable 1:1 complexes with all the transition metals examined. Conversely, cyclic ligands **CL_{3,4}** exhibit the unique property to specifically complex Cu(II) in the 1:1 ratio even in presence of sizeable amounts of Co(II) and Ni(II). The stoichiometry of the complexes was ascertained by microanalytical data [elemental analysis (EA) and atomic absorption (AA)] and confirmed by FAB MS spectrometry.

The IR spectra of the complexes are quite different from those of the free ligands, and give useful information on the possible binding sites involved in the coordination, according to the shift of the signals with respect to those of the free ligands, the most dramatic changes being observed in the 1600-1350 cm⁻¹ region. As a common feature, all the complexes examined display a very strong frequency band at 1385 cm⁻¹, indicating the participation of the nitrogens of at least one bipyridyl moiety in the complex formation. For the complexes of **AL₃**, **AL₄**, and **AL₅**, the carbonyl groups are undoubtedly involved in the complexation, as evidenced by a large shift ($\Delta\nu = 55\text{--}60\text{ cm}^{-1}$) of the carbonyl absorption to lower frequencies [13]. In the case of complexes **CL_{3a}** and **CL_{4a}**, the C=O stretching (Amide I band at 1631 and 1665 cm⁻¹, respectively) does not seem to be shifted as compared to the free ligands, indicating that it is not a binding site. On the other hand, for **CL_{4a}** we observe a $\Delta\nu = 11\text{ cm}^{-1}$ for the -NH stretching and a $\Delta\nu = 22\text{ cm}^{-1}$ for the -NH bending of the urea nitrogens, suggesting that they act as binding sites.

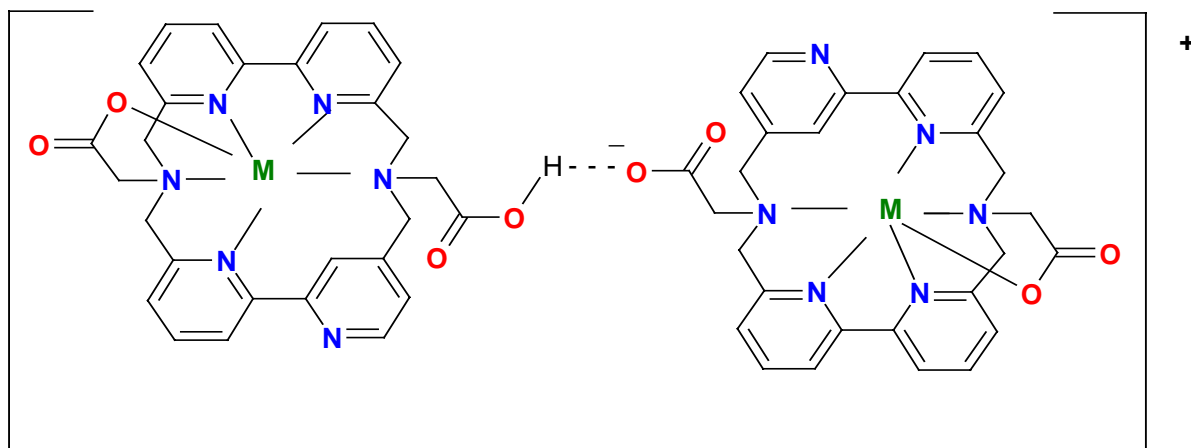
The synthesis of the complexes **AL_{5a-c}** was plagued by the competitive formation of a coloured side-product, obtained as a powder sparingly soluble in the reaction medium. These powders, also

insoluble in CH_2Cl_2 , were identified as dimeric complexes (**AL₆a-c**) formed by a new ligand (**AL₆**, R = COOH; Scheme 1), arising from a metal-induced hydrolysis of the ester functions [14].

The IR data of these complexes show: (i) a very intense and broad O-H stretching band at 3380 cm^{-1} , (ii) two C-H stretching bands at $2930\text{--}2985\text{ cm}^{-1}$, (iii) a C=O stretching band at 1680 cm^{-1} indicative of the presence of a free carboxylate anion, (iv) the lack of bands in the region $1750\text{--}1700\text{ cm}^{-1}$ (i.e. no resonance of the C=O group acting as binding site). These data may be consistent with a dimeric structure for these complexes composed of two monomeric subunits held together by a $\text{C(=O)O}^- \cdots \text{HOC(=O)}$ hydrogen bond [supported by microanalytical data, and FAB-MS measurements]. Each monomer is mononuclear, probably adopting an octahedral geometry around the complexed ion, with bipyridine nitrogens and the β bridged nitrogens forming a square plane, while the pyridine nitrogens occupy the axial positions. The general formula of these complexes can be written as $[\text{Me}_2(\text{AL}_6)_2\text{H}](\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ being Me = Cu(II), Co(II), Ni(II) (Table III).

A similar behaviour was observed by reacting the ligand **CL₅** with the metal nitrate salts. This cyclic ligand is not able to coordinate any metal by itself, as **AL₅** do, but, also in this case, owing to the hydrolysis of the ester groups a new ligand **CL₆** (R = COOH; Scheme 1) was obtained that uses its two $-\text{COO}^-$ groups in two different ways: one as binding site for the metal, the other one to link, through a hydrogen bond, another similar structure. As a matter of fact the IR data of the complexes **CL₆a-c** show, *inter alia*, a resonance at $\nu = 1665\text{ cm}^{-1}$ due to C=O group indicating a dimeric form via an intermolecular hydrogen bonding between two mononuclear complexes, and a resonance at $\nu = 1626\text{ cm}^{-1}$ that can be attributed to the asymmetrical stretching of the carboxylate anion that acts as binding site.

Figure 3. Possible dimeric structure of **CL₆ a-c** complexes.



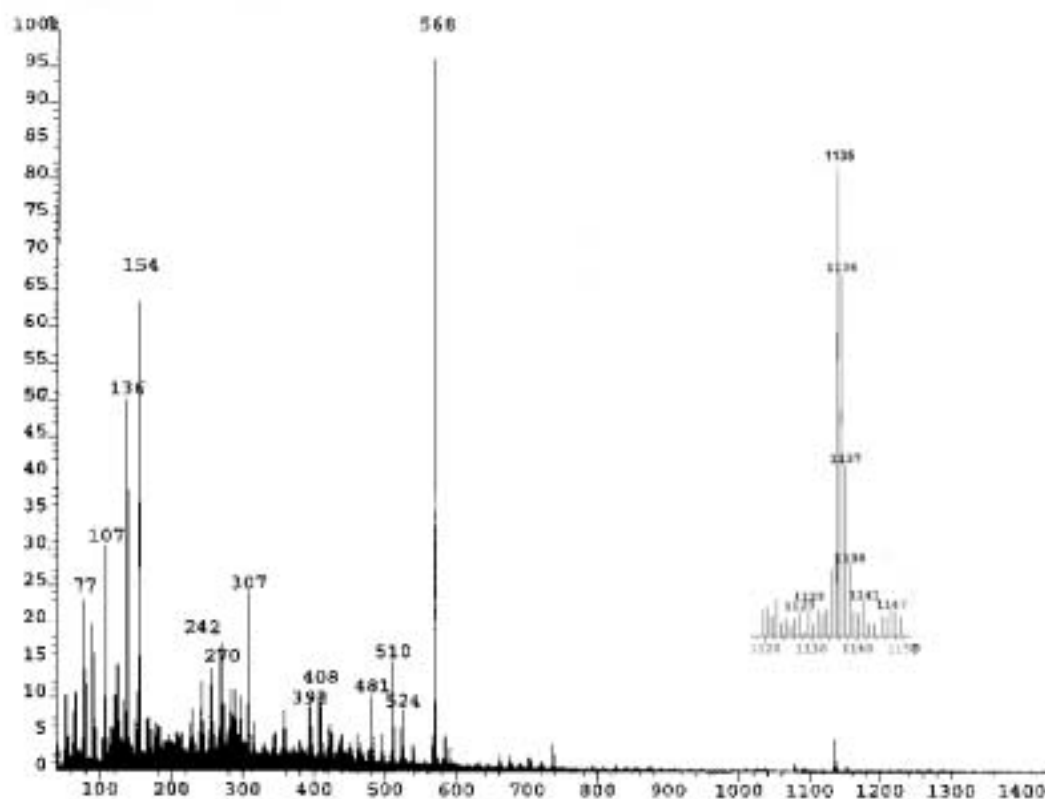
These dimeric crystalline complexes, **CL₆a-c**, of general formula $[\text{Me}_2(\text{CL}_6)_2\text{H}](\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$, were identified by FAB, AA, and EA. The dimeric structures for **CL₆a-c** complexes, hypothesized on the basis of their IR data, are corroborated by their FAB spectra, which show low intensity ion peaks at m/z 1143, 1135 and 1133, respectively, corresponding to $[(\text{CL}_6\text{Me})_2 - 3\text{H}]^+$, i.e. two mononuclear

complexes held together by a hydrogen bond forming between the carboxylate unit of one moiety and the carboxylic functionality of the other, as depicted in Figure 3.

Splitting of the dimers produces prominent peaks at m/z 572, 568 and 567, respectively, corresponding to $[\text{CL}_6\text{Me} - \text{H}]^+$ ions, which represent the base peak in the spectra of complexes **CL₆b,c**. In the case of **CL₆a** the base peak is found at m/z 573 ($[\text{CL}_6\text{Me}]^+$). Of note is the fact that no multicharged ion peaks could be detected in the FAB spectra of the complexes investigated. The observed isotopic patterns of all ion peaks are in good agreement with the calculated ones. The FAB spectrum of **CL₆b** is shown in Figure 4.

In Table III thermal gravimetric analysis (TGA) data of the synthesized complexes are reported. All complexes show a first degradation step, in the 40–50 °C range, corresponding to the loss of water/solvent molecules. **AL₃a-c** complexes show a second degradation step in the 100–110 °C range, that can be easily attributed to the loss of bound water ligand. The complexes with the acyclic ligands show, as expected, a decomposition temperature lower than that of the cyclic ones.

Figure 4. FAB mass spectrum of the $[\text{Co}_2(\text{CL}_6)_2\text{H}](\text{NO}_3)_3 \cdot 7\text{H}_2\text{O}$ complex (**CL₆b**)



Comparing the IR, FAB, and TGA data of the complexes bearing cyclic units to those of acyclic ones, we observe that the binding sites are different owing to the rigidity of cyclic structures that influence the complexing properties of the corresponding free ligands. It is known that the free bipyridyl moiety assumes an *anti* configuration that changes to *syn* when it works as bidentate binding site [15].

If this behaviour is easily hypothesized for the flexible acyclic ligand series, it may not be true for the cyclic one, because both bipyridyl units should assume the more favorable *syn* orientation for the complexation. This is why the **CL**₃ and **CL**₄ cyclic ligands are able to complex only the Cu(II) cation even if Co(II) or Ni(II) cations are present, due to the fact that the latter prefer an octahedral geometry that cannot be met with the rigid cyclic ligands; on the contrary the Cu(II) can be complexed owing to its ductility to assume different geometries. It is noteworthy that the cyclic ligand **CL**₆ (arising from the hydrolysis of **CL**₅) does not show any particular selectivity for the cations under study, probably due to its flexibility and to the presence of the –COOH groups that, working as binding sites, meet the Co(II) and Ni(II) geometric needs, unlike the rigid amido and ureido moieties present in **CL**₃ and **CL**₄, respectively.

Conclusions

Following our interest in macromolecular complexes bearing bipyridine chelating units, we have synthesized a series of *N,N'*-disubstituted acyclic (**AL**) and cyclic (**CL**) ligands, which can be viewed as model compounds for the related polymers, along with their complexes with Cu(II), Co(II), and Ni(II) transition metal ions. Dynamic ¹H-NMR studies on diurea and diamide derivatives point to the presence of slowly interconverting conformers on the ¹H-NMR time-scale. The complexing behaviour of the acyclic ligands was found to be different with respect to the cyclic ones. The former, following an easy *anti* to *syn* reorganization of the bipyridyl unit, give stable 1:1 complexes, while the latter, owing to their rigidity, show the unique property of recognising and binding copper(II) ion even in the presence of cobalt(II) and nickel(II) ions. A metal catalyzed hydrolysis of the ester groups was also observed, leading to the formation of dimeric structures linked by intermolecular hydrogen bonds.

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Experimental

General

Diamines **AL**₁ and **CL**₁, and their benzoyl derivatives **AL**₃ and **CL**₃, were synthesized according to literature procedures [2,6,9]. Anhydrous solvents were purchased from Fluka, and used without further purification. All reactions were conducted under a N₂ atmosphere. Melting points were determined on an Electrothermal melting point apparatus and are uncorrected. Elemental analyses were obtained commercially. ¹H-NMR spectra were performed in TCE with a Varian INOVA 500 instrument, using TMS as an internal standard. The ¹H-NMR spectra of all compounds synthesized are collected in

Tables II and III. FAB (+) MS spectra were taken on a Kratos MS 50 S double-focusing mass spectrometer equipped with a standard FAB source, using 3-nitrobenzyl alcohol as a matrix. IR spectra (KBr disks) were recorded on a Perkin Elmer 684 Infrared Spectrophotometer. AA measurements were obtained on a Perkin Elmer AAnalyst 300. The appropriate amount of the considered complex was destroyed with conc. HNO₃ (50 mL) and then diluted to 1 L with distilled water. Metal concentrations of such solutions were measured with a multielement hollow cathod lamp, by an oxidizing air-acetylene flame. Two standard solutions (concentrations of 0.5 and 1 ppm, respectively) were prepared for each metal by dissolving the metal compound (BDH Chemical Ltd. Laboratory Reagent Standards) in diluted HNO₃. Thermogravimetry was performed under nitrogen employing a Mettler TA 3000 thermogravimetric analyzer coupled with a Mettler TC 10 A processor at a heating rate of 10 °C/min.

N,N-Diacetyl-6,6'-Bis{[(2-pyridylmethyl)amino]methyl}-2,2'-bipyridine (**AL**₂).

A chilled solution of diamine **AL**₁ (59 mg, 0.15 mmol), Ac₂O (31 mg, 0.3 mmol) and Et₃N (0.3 mL) in dry CHCl₃ (2 mL) was stirred for 3 h. After quenching with water (1 mL), the reaction mixture was extracted with CHCl₃, washed with water and dried (MgSO₄). The solvent was evaporated to give an oily residue, which was subjected to column chromatography (neutral alumina, eluent: 3:1cyclohexane-AcOEt), to afford diamide **AL**₂ (53 mg, 85%) as white prisms, m.p. 129-130 °C (cyclohexane-CH₂Cl₂); FAB (+) MS, *m/z* 481 [MH]⁺; Anal. Calcd. for C₂₈H₂₈N₆O₂: C, 69.98; H, 5.87; N, 17.49. Found: C, 70.25; H, 5.64; N, 17.76

N,N-Diacetyl-2,17-diaza[3.3](6,6')-2,2'-bipyridinophane (**CL**₂).

A mixture of macrocyclic diamine **CL**₁ (79 mg, 0.2 mmol), Ac₂O (41 mg, 0.4 mmol) and Et₃N (0.4 mL) in dry CHCl₃ (20 mL) was stirred at r.t. for 5 h. The solvent was evaporated to leave a solid residue, which was washed with water and dried. Recrystallization from dimethylsulfoxide provided diamide **CL**₂ as colorless microcrystals (76 mg, 80%), m.p. >250 °C; FAB (+) MS, *m/z* 479 [MH]⁺; Anal. Calcd. for C₂₈H₂₆N₆O₂: C, 70.28; H, 5.48; N, 17.56. Found: C, 69.97; H, 5.40; N, 17.82.

N,N-Di(phenylureido)-6,6'-Bis{[(2-pyridylmethyl)amino]methyl}-2,2'-bipyridine (**AL**₄).

To a vigorously stirred and ice-chilled solution of diamine **AL**₁ (0.89 g, 2.25 mmol) in dry CHCl₃ (10 mL) was added dropwise a solution of phenyl isocyanate (0.54 g, 4.5 mmol) in dry CHCl₃ (5 mL). The mixture was allowed to stir at rt for 24 h. After evaporation of the solvent, the residue was dissolved in CH₂Cl₂ and purified by column chromatography (neutral alumina, cyclohexane-AcOEt 1:1 as an eluent) to give **AL**₄ (1.07 g, 75%) as white crystals, m.p. 160-161 °C (cyclohexane-AcOEt); FAB (+) MS, *m/z* 635 [MH]⁺; Anal. Calcd. for C₃₈H₃₄N₈O₂: C, 71.90; H, 5.39; N, 17.65. Found: C, 71.74; H, 5.11; N, 17.59.

N,N-Di(phenylureido)-2,17-diaza[3.3](6,6')-2,2'-bipyridinophane (**CL₄**).

Reaction of **CL₁** with phenyl isocyanate under conditions similar to those above described for the preparation of **AL₄** afforded derivative **CL₄** (64%) as fine needles, m.p. > 260 °C (DMF); FAB (+) MS, *m/z* 633 [MH]⁺; **Anal.** Calcd. for C₃₈H₃₂N₈O₂: C, 72.13; H, 5.10; N, 17.71. Found: C, 72.02; H, 5.15; N, 18.11

N,N-Di(*t*-butoxycarbonylmethyl)-6,6'-Bis{[(2-pyridylmethyl)amino]methyl}-2,2'-bipyridine (**AL₅**).

A solution of *t*-butyl-bromoacetate (0.69 g, 3.55 mmol) in dry CH₃CN (10 mL) was added dropwise to a stirred mixture of diamine **AL₁** (0.7 g, 1.76 mmol) and anhydrous K₂CO₃ (1.0 g, 7.4 mmol) in dry CH₃CN (10 mL). The mixture was then refluxed for 3 h under N₂, and allowed to stir at r.t. for an additional 12 h. The precipitate obtained was collected by filtration, thoroughly washed with water and dried. The solid was purified by column chromatography (neutral alumina, eluent: 3:1cyclohexane-AcOEt) to afford **AL₅** (0.88 g, 80%) as white crystals, m.p. 141-142 °C (EtOH); FAB (+) MS, *m/z* 625 [MH]⁺; **Anal.** Calcd. for C₃₆H₄₄N₆O₄: C, 69.20; H, 7.10; N, 13.45. Found: C, 68.89; H, 7.49; N, 13.05.

N,N-Di-(*t*-butoxycarbonylmethyl)-2,17-diaza[3.3](6,6')-2,2'-bipyridinophane (**CL₅**)

Reaction of **CL₁** with *t*-butyl-bromoacetate (2 equiv) under conditions similar to those described above for the preparation of **AL₅** afforded derivative **CL₅** (71%) as white crystals, m.p. 225-226 °C (cyclohexane-AcOEt); FAB (+) MS, *m/z* 623 [MH]⁺; **Anal.** Calc. for C₃₆H₄₂N₆O₄: C, 69.43; H, 6.80; N, 13.50. Found: C, 69.09; H, 6.73; N, 13.42.

Synthesis of complexes AL_{5a-c}, AL_{6a-c}, CL_{4a}, and CL_{6a-c}.

The synthesis of complex **AL_{4a}** is given as an example of the general complexation reaction procedure used for the preparation of complexes **AL_{5a-c}**, **AL_{6a-c}**, **CL_{4a}**, and **CL_{6a-c}**.

A slurry of **AL₄** (63.4 mg, 0.1 mmol) and Co(NO₃)₂·6H₂O (or Ni(NO₃)₂·6H₂O, or Cu(NO₃)₂·3H₂O) (0.1 mmol) in 1:1 MeOH/H₂O (6 mL) was stirred at room temperature for 48 h until a clear solution was obtained. The solution was concentrated to about 3 mL, and when left standing, crystals of the desired complex were obtained, which were collected by filtration and dried in vacuo. The analytical and physicochemical data of the complexes are given in Table III.

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Sample Availability: Available from the authors