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Synthesis, Coordination Properties, and Analytical Applications of Mixed Donor Macrocycles Containing the 1,10-Phenanthroline Sub-unit

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The coordination properties towards different metal ions of a new class of mixed N/S-, and N/S/O-donor macrocycles containing the 1,10-phenanthroline sub-unit in the cyclic framework are reviewed. The conformational constraints imposed by the heteroaromatic fragment onto the aliphatic portion of the ring determine the coordination mode of these ligands which can stabilise low-valent Ni⁺, Pd⁺, Pt⁺, and Rh⁺ metal complexes. Structural and thermodynamic aspects of the coordination chemistry of these ligands are considered together with possible applications as building blocks in the synthesis of multi-centred systems, and as template in the construction of extended polyiodide networks. However, solution studies demonstrate the inability of these ligands to work as selective and specific fluorescent chemosensors for heavy transition and post-transition metal ions and the formation constants evaluated for the formation of 1:1 complexes with Pb²⁺, Cd²⁺, Hg²⁺, Cu²⁺, and Ag⁺ in acetonitrile are of the same order of magnitude. Nevertheless, some of these macrocyles are extremely effective to recognise Cu²⁺ or Ag⁺ over the other metal ions in transport processes, and have been successfully used as neutral ionophore in the construction of PVC-based ion-selective electrodes and supported liquid membranes for analytical detection and separation, respectively, of these metal ions.

Keywords: Macrocyclic ligands, 1,10-Phenanthroline, Coordination properties, Ion-selective electrodes, Supported liquid membranes, Copper(II) and Silver(I)

INTRODUCTION

Following the pioneering work of 1987 Nobel Prize Winners C.J. Pedersen, D.J. Cram, and J.-M. Lehn, macrocyclic chemistry has developed into one of the most active areas of chemical science with implications in a wide variety of fields: the development of some fundamental aspects of "Supramolecular Chemistry" such as "molecular recognition", "host-guest interactions", and design of sensors and smart artificial "molecular devices" is strictly linked to the study of macrocyclic chemistry [1-3]. More and more sophisticated macrocyclic systems differing in molecular shape, architecture, arrangement of structural groups, binding sites, and reactive functions are continuously designed and synthesised with the aim to achieve control over strength, selectivity, and dynamics of the binding processes to substrates of different nature.

In particular, the design of novel macrocyclic chemical structures capable of specific and effective molecular recognition of metal ions is of vital importance to broad areas of analytical chemistry and separation sciences [4]. Selectivity of macrocyclic ligands in binding to metal ions can be finely

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tuned either by incorporating different soft and hard donor atoms in the chelating ring, or by modifying the flexibility properties of the macrocyclic structure introducing, for example, rigid sub-units in the chelating ring.

Due to the specific complexing abilities of crown ethers towards hard Group I and II metal ions, these ligands have been used as neutral carriers for the construction of PVCbased ion selective electrodes (ISEs) for alkali and alkaline earth metal cations, and for performing selective separations [5,6]. On the other hand, thioether macrocycles have come to great prominence in the last decade due to their selective and peculiar coordination properties towards soft transition metal ions and coinage metals, in particular [7,8], and numerous analytical applications have appeared [9-12].

In between these two classes of compounds, many mixeddonor host macrocyclic chemical structures, also featuring rigid sub-units in the chelating ring, have been designed and synthesised for a variety of guest compounds, and successfully used for analytical purposes [1,2,4,13-22]. In particular, π acceptor and redox- and photo-active 1,10-phenanthroline (phen) and 2,2'-bipyridine moieties have been either connected as side arms or incorporated into Schiff-base aza macrocycles, poly-aza macrocycles, crown ethers, cryptands and catenands as nonpendant integral part of the macrocyclic architecture, to give not only excellent multidentate structures capable of stabilising low-valent metal complexes and/or ligand-radical species, but also efficient sensing agents for ion-selective electrodes, fluorimetry, and selective ion transport across organic membranes [4,13,23-33]. In this context we have been engaged in the last decade in the development of a new class of mixed N/O/S-donor macrocycles featuring a phen sub-unit as an integral part of the macrocyclic structure (Fig. 1). Our initial aim was to combine the peculiar coordinating properties of phen with those of aliphatic thioether crowns. The results achieved by studying the coordination properties both in solution and in the solid state towards a variety of metal ions, and the analytical application of such new systems (mainly L^1-L^3 in Fig. 1) will



Fig. 1. Summary of Ligands.

be here reviewed.

SYNTHESIS AND CONFORMATIONAL CHARACTERISTICS

The strategy adopted in the synthesis of L^1-L^7 involves first the oxidation of 2,9-dimethyl-1,10-phenanthroline to the corresponding dialdehyde followed by its reduction to 2,9bis(hydroxymethyl)-1,10-phenanthroline and subsequent chlorination of the latter to 2,9-bis(chloromethyl)-1,10phenanthroline [34]. A cyclisation reaction performed under high dilution conditions between the dichloro derivative of 1,10-phennathroline and the appropriate dithiol in DMF in the presence of Cs₂CO₃ affords the required macrocylic ligand with yields ranging from 20% (L^4) to 69% (L^1) [35-39]. Crystals of $L^2 \cdot \frac{1}{2}H_2O$ and $L^3 \cdot H_2O$ were grown from a MeCN/Et₂O solution [36,47]. The structure of $L^2 \cdot \frac{1}{2}H_2O$ shows the presence of two independent macrocyclic molecules in the asymmetric unit, one of which exhibiting disorder in the aliphatic portion of the ring. Analogous disorder is observed in the independent molecule of L^3 in the asymmetric unit of $L^{3}\cdot H_{2}O$.

Molecular mechanics calculations (MM) were performed on L^1 - L^3 in order to understand better the conformational behaviour of these new phenanthroline-based macrocycles [36,47]. Two features are common to all conformers calculated for L^1 - L^3 : (a) the aliphatic portion of the ring is folded over the plane of the phenanthroline unit; (b) in the conformations which have calculated the lowest conformational energies (the eight most stable have been considered), the lone-pairs on the S- and O-donors tend to adopt exodentate orientations pointing out of the macrocyclic cavity. Compared to L^1 and L^2 , the replacement of the O(S)donor with a methylene group in L^3 causes a slight increase in the flexibility of the aliphatic chain connected to the phenanthroline unit. In fact, the torsion angles S-C-C-X, which in the case of L^1 (X = S) and L^2 (X = O) assume *anti* arrangements in the most stable calculated conformers, can also assume a gauche disposition in L^3 (X = CH₂). Furthermore, the torsion angles about the C-X bonds, which, apart from few exceptions, are generally one gauche and one anti in L^1 and L^2 , can be both anti and both gauche for the most stable conformers calculated for L^3 . A less regular trend is also observed for the torsion angles about the C–S bonds, which are preferentially *gauche* in the most stable conformers calculated for L^1 and L^2 .

Interestingly, the conformation adopted by the undisordered independent molecule of L^2 in the crystal structure of L^2 .¹/₂H₂O is very similar to the most stable conformer calculated for L^2 , while that adopted by the other independent molecule, considering the major component of the disorder model, is practically identical to the second most stable calculated conformer [36]. Analogous similarities are found between the first and sixth most stable conformers calculated for L^3 and, respectively, the conformations adopted by the major and minor disorder components observed in the independent molecule of L^3 in the asymmetric unit of L^3 ·H₂O [47].

On these grounds, it appears clear, therefore, that in these new macrocyclic ligands the phenanthroline sub-units strongly affects the conformational flexibility of the aliphatic portion of the ring, and conformational pre-organisation is expected prior to complexation to metal ions in order for the lone-pairs on the donor atoms in the aliphatic chain to point into the macrocyclic cavity.

COORDINATION PROPERTIES

Nickel(II)

The first studies on the coordination chemistry of these new mixed thia-aza macrocyclic ligands were performed towards d^8 transition metal ions, Ni²⁺ in particular. In $[Ni(L^1)(MeCN)][BF_4]_2$, obtained by reacting NiCl₂·6H₂O with L^1 (1:1 molar ratio) in acetonitrile (MeCN)/H₂O followed by addition of excess NH₄BF₄, the macrocyclic ligand acts as an N₂S₃ pentadentate donor encapsulating the metal centre within a cavity having a square-based pyramidal stereochemistry, with an MeCN molecule completing an overall distorted octahedral coordination sphere around the Ni²⁺ ion (Fig. 2a) [35]. As expected, the S-donors in L^1 adjacent to the phen moiety assume endo dentate orientations upon complexation, with the aliphatic portion of the ring folded over the plane of the heteroaromatic sub-unit. Interestingly, the complex $[Ni_2(Cl)_2(L^4)_2][BF_4]_2$ ·3MeNO₂ shows a dichloro bridged binuclear structure (Fig. 2b) with L^4 bound via only two Sand two N-donors and the remaining two thioether S-donors



Fig. 2. (a) $[Ni(L^1)(MeCN)]^{2+}$; (b) $[Ni_2(L^4)_2(Cl)_2]^{2+}$ [35].

unbound [35]. As compared to L^1 , this situation clearly reflects the inability of L^4 to occupy five coordination sites of a distorted octahedral coordination sphere.

The MeCN molecule in $[Ni(L^1)(MeCN)]^{2+}$ can easily be replaced by other ligands offering a useful route to different pseudo-octahedral mononuclear complexes of the type $[Ni(L^1)(L')]^{(2-n)+}$, where (2-n) depends on the charge of L'. Initially, this substitution reaction was followed by UV-Vis spectrophotometric titrations, carried out in MeCN solutions, using mono-anionic [Cl⁻, Br⁻, I⁻, CN⁻, SCN⁻, N₃⁻ with n = 1] and neutral ligands L' [H₂O, 4,4'-bipyridine (4,4'-bipy), pyridine (py), aniline (an), 1,3-dimethyl-4-imidazoline-2thione (etu), 1,3-dimethyl-4-imidazoline-2-selone (eseu), n =0] [40,41]. While the substitution reaction of the coordinated MeCN molecule in $[Ni(L^1)(MeCN)]^{2+}$ with all considered mono-anionic ligands L' is quantitative with neat inflection points in the titration curves at the 1:1 $[L']/[Ni(L^1)(MeCN)]^{2+}$ molar ratio; for the neutral ones, the substitution process is governed by the equilibrium:

$$[\operatorname{Ni}(\mathbf{L}^{1})(\operatorname{MeCN})]^{2+} + \mathbf{L}' \longrightarrow [\operatorname{Ni}(\mathbf{L}^{1})(\mathbf{L}')]^{2+} + \operatorname{MeCN} (1)$$

The corresponding equilibrium constants calculated from a non-linear least-square method, indicate a py > 4,4'-bipy >

 $H_2O > eseu > etu > an donor order for the chosen neutral$ ligands L' [40,41]. The compounds [Ni(L¹)(Cl)]BF₄·DMF,[Ni(L¹)(I)]I₃, [Ni(L¹)(Cl)]Cl·H₂O, [Ni(L¹)(SCN)]BF₄·MeNO₂,[Ni(L¹)(N₃)]BF₄, [Ni(L¹)(H₂O)][ClO₄]₂·H₂O, [Ni(L¹)(py)][BF₄]₂, and [Ni(L¹)(eseu)][BF₄]₂ were also isolated as singlecrystals and characterised by X-ray diffraction analysis. In allcases, an [N₂S₃ + L'] distorted octahedral coordination isobserved at the metal centre with the macrocyclic ligandalways adopting the typical locked-folded conformation[35,40,41].

Interestingly, the reaction in acetonitrile (MeCN) of $[Ni(L^1)(L')][BF_4]_{(2-n)}$ (L' = MeCN, Cl⁻, Br⁻, I⁻) with I₂ in different stoichiometric amounts in the presence/absence of the stoichiometric amount of I⁻ necessary to balance the charge of the complex cation $[Ni(L^1)(L')]^{(2-n)}$ gave, independently of the nature of L', the compounds $[Ni(L^1)(MeCN)]I_8$ and $[Ni(L^1)(MeCN)]I_{12}$ which feature interesting polyiodide networks [42]. Therefore, the complex cation $[Ni(L^1)(MeCN)]^{2+}$ acts as template of the two different polyiodide networks based on interacting I_3^-/I_5^- and I_5^-/I_7^- , respectively.

The electrochemistry of most of the prepared monomeric Ni^{2+} complexes with L^1 was studied by cyclic voltammetry [40]. In particular, the reductive cyclic voltammetry of $[Ni(L^1)(MeCN)][BF_4]_2$ in MeCN shows a quasi-reversible one

electron reduction wave at ${}^{1}E_{\nu_{2}} = -0.98 \text{ V } vs. \text{ Fc/Fc}^{+}$, and a second broad irreversible process at ${}^{2}E_{\text{pc}} = -1.91 \text{ V}$. Electrochemical reduction by controlled-potential electrolysis at the first reduction potential in the presence of the lignd PMe₃, and investigation of the reduced product by ESR spectroscopy, confirmed the formation of the species $[\text{Ni}^{\text{I}}(\mathbf{L}^{1})(\text{PMe}_{3})]^{+}$. This clearly indicates that the first reduction wave in the cyclic voltammogram of $[\text{Ni}(\mathbf{L}^{1})(\text{MeCN})]^{2+}$ is metal based (*i.e.* Ni^{II} \rightarrow Ni^I) and corresponds to the initial formation of the species $[\text{Ni}^{\text{I}}(\mathbf{L}^{1})]^{+}$ rather than to the formation of a Ni²⁺ ligand radical species $[\text{Ni}^{\text{II}}(\mathbf{L}^{1-})]^{+}$. Furthermore, it indicates that \mathbf{L}^{1} is able to stabilise low-valent metal complexes thanks to the excellent π acceptor properties of the phen sub-unit.

In the absence of PMe₃, a brown ESR silent precipitate is formed under controlled-potential electrolysis in MeCN on the first reduction peak of $[Ni(L^1)(MeCN)]^{2+}$, presumably a binuclear complex having a Ni^I-Ni^I bond, as observed for Ni⁺ complexes with tetraaza-macrocyclic ligands [40]. CV measurements on most of the complexes obtained from $[Ni(L^{1})(MeCN)]^{2+}$ by substituting the coordinated MeCN molecule with anionic ligands were carried out in DMF for solubility reasons. The first reduction wave is completely irreversible and the substantial variation of ${}^{1}E_{pc}$ (from -1.18 to -1.48 V vs. Fc/Fc⁺) on changing the nature of the anionic ligand L' represents a further evidence of the reduction process being metal based. CV measurements carried out in DMF in the cases of $[Ni(L^1)(L')]^{2+}$ complexes obtained from $[Ni(L^{1})(MeCN)]^{2+}$ with neutral ligands L' show the first reduction process to be quasi-reversible and to have a narrow range of variability for ${}^{1}E_{pc}$ (between -1.11 and -1.23 V vs. Fc/Fc⁺). This was attributed to equilibrium (1) which occurs in MeCN as well in DMF solution [40].

Since L^1 blocks five sites of an octahedral coordination sphere around Ni²⁺, the aforementioned substitution of the coordinated MeCN molecule in [Ni(L¹)(MeCN)]²⁺ could, in principle, allow the synthesis of Ni²⁺-multinuclear complexes [{Ni(L¹)}_mL']^{(2m-n)+} having a single bridging exogenous multidenate ligand L'. In order to verify this, [Ni(L¹)(MeCN)]²⁺ was reacted in MeCN with NaN₃, 4,4'-bipy, and Bu₄NF·H₂O in a 1:0.5 molar ratio with the aim to synthesize Ni²⁺-binuclear complexes [41]. The mononuclear complex [Ni(L¹)(N₃)]⁺ was the only product formed in



Fig. 3. $[{Ni(L^1)}_2F]^{3+}$ [41].

solution and in the solid state (as single crystals suitable for Xray diffraction analysis, see above) either using a 0.5:1 or 1:1 NaN₃/[Ni(L¹)(MeCN)]²⁺ reaction molar ratio [41]. Interestingly, upon addition of 4,4'-bipy to $[Ni(L^1)(MeCN)]^{2+}$ in MeCN, only the 1:1 mononuclear species was formed in solution over the whole range of reaction molar ratios (from 0 to 10), despite the fact that the relatively insoluble binuclear complex [{Ni(L¹)}₂(4,4'-bipy)]⁴⁺ was the only species isolated in the solid state (as micro-crystals) using either a 0.5:1 or a 1:1 4,4'-bipy/[Ni(L¹)(MeCN)]²⁺ reaction molar ratio [41].

Using F^- as bridging ligand, the formation of a Ni²⁺binuclear species was observed both in solution and in the solid state, and single crystals corresponding to the formulation $[{Ni(L^1)}_2F][BF_4]_3$ ·MeCN·H₂O were grown and studied by X-ray diffraction [41]. In this single F-bridged Ni²⁺-dimer (the second of this type ever reported, and the first magnetically characterised showing а significant antiferromagnetic exchange), the phen moieties of the two $[Ni(L^{1})]^{2+}$ units face each other and lies on almost parallel planes at a mean distance of about 3.70 Å (Fig. 3). However, the $[Ni(L^1)]^{2+}$ units are rotated with respect to each other along the Ni-Ni' axis and the projection of one phen moiety does not superimpose on the top of the other.

The weak π - π interaction between the phen moieties in $[{Ni(L^1)}_2F]^{3+}$ might explain why only mononuclear Ni²⁺ complexes are isolated from the reaction of $[Ni(L^1)(MeCN)]^{2+}$



Fig. 4. (a, b) $[Pd(L^1)]^{2+}$ [43].

with the larger Cl⁻, Br⁻, and I⁻ halogenide anions. Indeed, an almost linear μ -Cl, μ -Br, μ -I bridge between two $[Ni(L^1)]^{2+}$ units would set the two phen moieties too far away from each other, thus hampering any π - π interaction between the two aromatic systems.

The possibility of using the $[Ni(L^1)]^{2+}$ cation from $[Ni(L^1)(MeCN)]^{2+}$ via substitution of the MeCN molecule, as a building block for the design of multi-centred compounds with multidentate bridging ligands, is still an on going research in our laboratories.

Also the compound $[Ni(L^2)Cl]BF_4$, obtained by reacting NiCl₂·6H₂O with L^2 (1:1 molar ratio) in MeCN/H₂O followed by addition of excess NH₄BF₄, was structurally characterised [36]. Although no significant differences are observed in the conformation adopted by L^1 and L^2 upon complexation with Ni²⁺, the presence of an harder O-donor instead of a softer S-donor *trans* to the coordination site left free by the pentadentate macrocyclic ligands drives the formation $[Ni(L^2)Cl]^+$ instead of $[Ni(L^2)(MeCN)]^{2+}$. As contrary to what is observed for the MeCN molecule in the $[Ni(L^1)(MeCN)]^{2+}$ cation, the chloride donor in $[Ni(L^2)Cl]^+$ cannot easily be substituted by direct reaction with other neutral or charged donors, thus preventing the use of the $[Ni(L^2)]^{2+}$ cation as building block for more complex systems.

Palladium(II), Platinum(II), Ruthenium(II), and Rhodium(III)

The coordination chemistry of L^1 and L^2 was also

investigated towards the titled $d^{6/8}$ transition metal ions.

For all of them, the corresponding 1:1 metal complexes were isolated and in some cases structurally characterised [36,43,44].

In $[M(L^1)][BF_4]_2$ (M = Pd²⁺, Pt²⁺) [43] and $[Pd(L^2)][BF_4]_2$ compounds [the latter was crystallised in both the triclinic and monoclinic (with two molecules of MeCN co-crystallised per unit cell) systems] [36], the metal ions satisfy their preference for a square-planar coordination geometry through the two Ndonors from the phen moiety and two S-donors from the aliphatic portion of the macrocyclic ligands (Figs. 4, 5). The remaining S- and O-donor atoms in L¹ and L², respectively, weakly interact with the metal centres trying to occupy the apical position of a square-based pyramid in a formal [4 + 1] coordination sphere.

The Pd···S_{ap} long-range interactions in $[Pd(L^1)]^{2+}$, 2.865(1) Å (Figs. 4) [43] is significantly shorter than the Pd···O separation, 2.935(4) Å, in the $[Pd(L^2)]^{2+}$ complex cation (triclinic crystals, Fig. 5a) [36]; furthermore, the Pd···S_{ap} vector in $[Pd(L^1)]^{2+}$ shows a deviation of only 14.3° from perpendicularity with respect to the Pd²⁺ coordination plane, as compared to a deviation of 34.3° observed for the Pd···O vector in $[Pd(L^2)]^{2+}$. This is consistent with the greater preference of Pd²⁺ and Pt²⁺ for soft donors; however, the coordination geometry of the Pd²⁺ and the disposition of the ligand L^2 (the lone pair on the O atom is clearly oriented towards the d_z^2 orbital of the palladium) indicate that some form of apical interaction between the metal centre and the O-

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Fig. 5. (a) $[Pd(L^2)]^{2+}$ (triclinic form); (b) $[Pd(L^2)]^{2+}$ (monoclinic form) [36].

donor of the ligand is present in $[Pd(L^2)]^{2+}$ (triclinic crystals, Fig. 5a). This interaction is very weak as indicated by NMR studies (*vedi infra*) and by the even higher Pd···O separation, 3.01(2) Å, observed in the monoclinic crystals of $[Pd(L^2)]^{2+}$ (Fig. 5b) with the Pd···O vector deviating by 36.2° from perpendicularity with respect to the palladium coordination plane [36].

Furthermore the O-donor in the monoclinic crystals is disordered over two sites with the minor component of the disorder model oriented away from the axial site of the N₂PdS₂ coordination plane (Fig. 5b). These structural features of the complex cations $[Pd(L)]^{2+}$ ($L = L^1$ and L^2) clearly demonstrate the inability of the aliphatic CH₂CH₂XCH₂CH₂ (X = S, O) fragment to orient itself as to encapsulate fully the axial site of a square pyramidal coordination geometry around the metal centre; this could be attributed to both the weakness of the interaction between the O(S)-donor and the metal ion and the geometrical constraints imposed by the phen unit on the aliphatic portion of the macrocyclic ligands [in this respect, the Pd…S_{ap} distances in $[Pd(L^1)]^{2+}$ is shorter of the Pt…S_{ap} one, 2.938(1) Å, in $[Pt(L^1)]^{2+}$ as contrary to what expected on the basis of electronic effects] [43].

With Ru^{2+} and Rh^{3+} , the compounds $[Ru(L^1)Cl]Cl\cdot4H_2O$ [36], $[Ru(L^2)(PPh_3)][PF_6]_2\cdot\frac{1}{4}MeCN$ [36], $[Rh(L^1)Cl][PF_6]_2\cdot$ 2MeCN [44], and $[Rh(L^2)Cl_2]BF_4$ [36] were synthesised and the first three also structurally characterised (Fig. 6). Interestingly, a complex cation corresponding to the formulation $[Rh(L^1)Cl_2]^+$ was demonstrated by cyclic voltammetry to be responsible of the assisted transfer of Rh^{3+} at the polarised water/1,2-dichloroethane junction by interfacial coordination with L^{1} [44].

As expected, analogously to the case of Ni²⁺, both L¹, and L² assume in these complexes with heavier Group VIII transition metal ions a folded conformation, with all donor atoms strongly coordinating, and encapsulating the metal centre within a cavity which confers a square-based pyramidal stereochemistry. An overall distorted octahedral coordination sphere is completed by a Cl⁻ ion *trans* to an S-donor in $[Ru(L^1)Cl]^+$ and $[Rh(L^1)Cl]^{2+}$, and by a triphenylphosphine ligand *trans* to the O-donor in $[Ru(L^2)(PPh_3)]^{2+}$.

The ¹³C NMR spectra for L^1 and L^2 and their complexes with Pd²⁺, Pt²⁺, Ru²⁺, and Rh³⁺ in CD₃CN solution in the range 320-238 K were also recorded [36,43]. The spectra of the complexes show no changes in any features of their peaks (six for the aromatic region and three for the aliphatic portion of the macrocyclic ligands, a C_s symmetry is supposed for the form present in solution) over the temperature range explored, demonstrating the absence of fluxionality in solution, but also excluding the possibility that the apical S-donor in L^1 or the O-donor in L^2 (Figs. 4-6) is flipping between being bound and unbound to the metal centres.

Furthermore, solid state ¹³C NMR spectra exhibit the same pattern as those in solution for all the complexes, with good agreement between the chemical shifts. With respect to the free macrocycles, the aliphatic C atoms bound to the phen subunits are deshielded whereas those next to the apical S-donor in the case of L^1 and next to O-donor in the case of L^2 are shielded for the complexes of Pd^{2+} , Pt^{2+} , and for $[Rh(L^2)Cl_2]^+$.



Fig. 6. (a) $[Ru(L^1)Cl]^+$; (b) $[Ru(L^2)(PPh_3)]^{2+}$ [36]; (c) $[Rh(L^1)Cl]^{2+}$ [44].

The situation is different for $[Rh(L^1)Cl]^{2+}$ and for the Ru²⁺ complexes in which all the above mentioned C atoms are deshielded. These data are consistent with the X-ray diffraction studies and in particular with both the O-donor being un-coordinated in $[Rh(L^2)Cl_2]^+$ (the two chloride ligands assuming a *trans* disposition), and a [4 + 1] coordination sphere being imposed by L^1 and L^2 at the Pd²⁺ and Pt²⁺ ions in the solid state as well in solution, with the apical S- (\mathbf{L}^{1}) and O-donors (L^2) weakly interacting with the metal centres. These conclusions, also confirmed by ¹H NMR data, clearly point out the reduced flexibility of this type of macrocycles in their complexes with the Group VIII transition metal ions considered; the ligands are therefore locked in a folded conformation by the stereoelectronic requirements of the metal ions and by the restraints imposed by the presence of the rigid phen sub-units. Furthermore, the substitution of the soft apical S-donor in L^1 with the hard O-donor in L^2 allows one to alter, and in principle to control the coordination environment around Group VIII transition metal ions. In particular, for metal ions preferring an octahedral coordination geometry $(Ni^{2+}, Ru^{2+}, Rh^{3+})$ the coordination at the sixty position left free by the macrocyclic framework can be controlled by substituting L^1 with L^2 , thus assisting the host-guest complexation process.

Cyclic voltammetry measurements (Table 1) of all complexes with heavy Group VIII transition metal ions here considered were carried out in MeCN ($0.1 \text{ M Bu}_{4}^{n}\text{MBF}_{4}$) at

platinum electrodes [36,43]. The first reduction process for the Pd^{2+} , Pt^{2+} , and Rh^{3+} complexes, and the second reduction process observed for the Rh^{3+} complexes were coulometically tested to be a one-electron exchange and assigned to the couples $Pd^{II/I}$, $Pt^{II/I}$, and $Rh^{III/II}$ and $Rh^{II/I}$, respectively, by comparison with the redox behaviour of related complexes with polythia and mixed N/S-donor macrocyclic ligands. Unfortunately, attempts to establish the precise nature of the reduction products in the case of Pd^{2+} and Pt^{2+} complexes were not successful, presumably because of their high reactivity [36,43]. Mononuclear Pd^{I} and Pt^{I} coordination compounds are highly unusual and dimerization involving metal-metal bond formation is described as the dominant quenching process [43].

In the case of Rh^{3+} complexes with L^1 and L^2 , the ESR spectra recorded as frozen (77 K) glasses on MeCN solutions obtained after reductive controlled-potential on the first reduction peak for both $[Rh(L^1)Cl]^{2+}$ and $[Rh(L^2)Cl_2]^+$, although of insufficient quality to derive reliable parameters, clearly indicated the presence of broad signals at low fields which are typical of Rh^{2+} species [36]. The reduction process observed for the complexes $[Ru(L^1)Cl]^+$ and $[Ru(L^2)(PPh_3)]^{2+}$ (Table 1) is instead considered ligand-centred by comparison with the electrochemical behaviour of the complexes $[Ru(Me_2-phen)_3]^{2+}$ and $[Ru(Me_2-bipy)_3]^{2+}$ characterised by three reversible one-electron reductions which were shown to correspond to successive reduction of the three coordinated

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Table 1. Redox Peaks vs. Fc/Fc⁺ Observed by Cyclic Voltammetry in MeCNSolution for all the L^1 and L^2 Complexes Synthesised with HeavyGroup VIII Transition Metal Ions (Supporting Electrolyte 0.1 M $Bu^n_4NB_4$, Scan Rates from 50 to 400 mV s⁻¹)^a

Complex cation	$E_{ m pa}$	${}^{1}E_{\rm pc}$	$^{2}E_{\rm pc}$	${}^{3}E_{\rm pc}$	Ref.
$[Pd(L^{1})]^{2+}$	+1.268	-0.733	-1.201	-	[43]
$[Pt(L^{1})]^{2+}$	+0.989	-1.174	-1.520	-	[43]
$[Pd(L^2)]^{2+}$		-0.83	-1.70	-	[36]
$[Pt(L^2)]^{2+}$	-	-1.32	-1.78	-	[36]
$[Rh(L^1)Cl]^{2+}$	-	-0.94	-1.26	-1.76	[36]
$[Rh(L^2)Cl_2]^+$	-	-0.94	-1.28	-1.67	[36]
$[Ru(L^1)Cl]^+$	+0.70	-1.73	-	-	[36]
$[Ru(L^{2})(PPh_{3})]^{2+}$	-	-1.60	-	-	[36]

^aAll redox peaks are irreversible; for $[M(L)]^{2+}$ (M = Pd²⁺, Pt²⁺; L = L¹, L²), the first irreversible reduction becomes quasi-reversible if the scan direction of the cyclic voltammogram is changed from cathodic to anodic before the onset of the second reduction process.

ligand molecules [45]. The same can be said for the third reduction process observed for the complexes $[Rh(L^1)Cl]^{2+}$ and $[Rh(L^2)Cl_2]^+$ (Table 1). The one-electron oxidation observed for $[Ru(L^1)Cl]^+$ occurs in the range typical for $Ru^{11/1}$ couples and disappears in $[Ru(L^2)(PPh_3)]^{2+}$ presumably due to the effect of the PPh₃ ligand stabilising the Ru^{2+} centre.

Overall these studies on the coordination chemistry of L^1 and L^2 towards Ni²⁺, Pd²⁺, Pt²⁺, Rh³⁺, and Ru²⁺ transition metal ions clearly point out the ability of these macrocyclic ligands to stabilise the corresponding low-valent metal complexes. This ability is a strict consequence of the conformational constraints imposed by the phen unit on the aliphatic linker of the ring, and by the nature of the donor set assembled in a peculiar cyclic framework. In particular, the Ni⁺, Pd⁺ and Pt⁺ complexes with L^1 and L^2 might be of interest in the field of catalysis due to the possibility for the encapsulated metal centre to reach an octahedral stereochemistry by interaction with an additional ligand.

Lead(II), Cadmium(II), and Mercury(II)

The presence of soft S-donors in the macrocyclic ligands L^1-L^7 and the well known photophysics properties of the phen sub-unit prompted us to study their coordination properties also towards toxic d^{10} soft metal ions such as Pb²⁺, Cd²⁺, and

Hg²⁺ in order to test the potentiality of these cyclic phenanthroline derivatives, L^1-L^3 in particular, as efficient complexing agents and selective extractants of these environmental important metal ions, and as fluorescent sensors for their detection in solution [38]. In fact, L^1 - L^3 as well as all the other ligands in Fig. 1 and the polyamine macrocycles reported by A. Bencini et al. [25,26,28,29,31-33] can be considered intrinsic fluorescent chemosensors with the thioether linkers functioning exclusively as binding sites and the phen unit playing both a signalling and a binding role. L^{1} - L^3 in MeCN show an absorption band at about 280 nm and a fluorescent band around 360 nm. The effect on the fluorescence intensity upon addition of increasing amounts of Pb^{2+} , Cd^{2+} , or Hg^{2+} to a MeCN solution of L^1 , L^2 , or L^3 was therefore investigated. The shape and position of the of the fluorescence emission bands do not change in the presence of the metal ions compared to those of free ligands, whereas the emission intensities change as function of the M^{2+}/L (M^{2+} = Pb^{2+} , Cd^{2+} , Hg^{2+} ; $L = L^{1-}L^{3}$) molar ratio according to the curves reported in Fig. 7.

A chelation enhancement of quenching of the fluorescence (CHEQ) is observed for all three ligands on addition of increasing amounts of Pb^{2+} and Hg^{2+} . From the inflection points in the fluorescence intensity/molar ratio plots it can be



Fig. 7. Fluorescent intensity/molar ratio plots for L^1 (a), L^2 (b), and L^3 (c) $(1.0 \times 10^{-5}$ M, MeCN, 25 °C) in the presence of increasing amounts of Pb²⁺, Cd²⁺, and Hg²⁺ [38].

inferred that 1:1 $[M(L)]^{2+}$ complexes $(M = Pb^{2+}, Hg^{2+}; L = L^1,$ L^{2}) are formed. The formation of $[M(L)_{2}]^{2+}$ species appears to take place only with L^3 for Pb²⁺ and with both L^1 and L^2 for Hg²⁺. A different trend of the fluorescence intensity variation is observed upon addition of Cd²⁺ to MeCN solution of the three ligands. A CHEQ effect followed by a chelation enhancement of fluorescence (CHEF) is observed with L^1 and L^{3} (Figs. 7a, c); the inflection points in the spectrofluorometric titration curves indicate the formation of the species $[Cd(L^1)]^{2+}\!\!,\ [Cd_2(L^1)]^{4+}\!\!,\ [Cd(L^3)]^{2+}\!\!,\ \text{and}\ [Cd(L^3)_2]^{2+}\!\!.$ In the case of L^2 (Fig. 7b) a CHEF effect is observed throughout the whole range of Cd^{2+}/L^2 molar ratios explored with formation of the 1:1 and 1:2 metal-to-ligand complexes. The species formed stoichiometry of the during the spetrofluorometric titrations was confirmed by conductometric measurements and by the best fitting of the experimental data to the appropriate complexation models which allowed evaluation of the corresponding formation constants (Table 2) [38]. Interestingly, a complex cation corresponding to the formulation $[Pb(L^3)_2]^{2+}$ was demonstrated by cyclic voltammetry to be responsible of the assisted transfer of Pb²⁺ at the polarised water/1,2-dichloroethane junction by interfacial coordination with L^3 [46].

Disappointingly, the stability constants for the 1:1 complexes of the three metal ions are of the same order of magnitude, and this, despite differences observed in the fluorescent intensity variation of the ligands with the three metal ions, clearly point out a totally absence of selectivity for the three ligands as fluorescent chemosensors of the soft d^{10} metal ions considered (this aspect will be re-considered in the second part of the review dealing with the analytical applications).

The complexation properties of L^{1} - L^{3} towards Pb^{2+} , Cd^{2+} , and Hg^{2+} were also investigated in the solid state. The reaction between the ligands and the metal ions always afforded 1:1 metal complexes, except the reaction of L^{3} with Pb^{2+} which always gave in the solid state a compound having a formulation corresponding to a 1:2 Pb^{2+}/L^{3} stoichiometry. Crystals suitable for X-ray diffraction analysis were obtained for the complexes $[Pb(L^{1})][ClO_{4}]_{2}$ · $^{1}/_{2}H_{2}O$, $[Pb(L^{2})][ClO_{4}]_{2}$ · MeNO₂ (Fig. 8), $[Pb(L^{3})_{2}][ClO_{4}]_{2}$ ·2MeCN, and $[Cd(L^{3})]$ $[NO_{3}]_{2}$ (Fig. 9) [38]. In all cases the three ligands adopt a folded conformation similarly to that observed in related

Ligand	Ion	$\log K_1^{b}$	$\log K_2^{c}$	Ref.
L^1	Pb ²⁺	7.5 (2)		[38]
	Cd ²⁺	5.53 (2)	$2.62(3)^{d}$	[38]
	Hg ²⁺	5.95 (16)	2.93 (12)	[38]
	Cu ²⁺	5.29 (4)		e
	Ag^+	7.2 (1) [7.2 (1), ^f 7.0 (2), ^g 7.2 (1) ^h]		[39]
L^2	Pb ²⁺	6.24 (5)		[38]
	Cd ²⁺	6.40 (9)	3.00 (9)	[38]
	Hg ²⁺	5.34 (15)	2.69 (12)	[38]
	Cu ²⁺	6.44 (7)		e
	Ag^+	8.4 (3) [8.3 (1), ^f 8.2 (2), ^g 8.5 (2) ^h]		[39]
L ³	Pb ²⁺	6.07 (6)	2.22 (6) ^{i, 1}	[38]
	Cd ²⁺	5.86 (4)	2.91 (3)	[38]
	Hg ²⁺	5.56 (4)		[38]
	Cu ²⁺	6.15 (6)		e
	Ag^+	$6.9(1)[6.8(1), 6.8(3), 6.9(1)^{h}]$		[39]
L^5	Ag^+	$6.65(7)[6.7(1),^{f}6.94(8)^{g}]$	$5.20(5)[5.4(1),^{f}5.27(3)^{g}]$	[39]
L ⁶	Ag^+	7.31 (5) $[7.3 (1), {}^{f}7.20 (9)^{g}]$	$5.47(2)[5.5(1),^{f}5.72(3)^{g}]$	[39]

Table 2. Stepwise Formation Constants^a of Pb²⁺, Cd²⁺, Hg²⁺, Cu²⁺ with L¹- L³ and of Ag⁺ with L¹-L³, L⁵ and L⁶ in MeCN at 25 °C Calculated by Fitting the Fluorescence/Molar Ratio Data

^aValues in parentheses indicate standard deviations. ^bM + L = ML. ^cML + L = ML₂. ^dThis value refers to the formation constant of the complex $[Cd_2(L^1)]^{2+}$: ML + M = M₂L. ^eV. Lippolis and M. Shamsipur unpubblished results. ^fFrom spectrophotometric measurements. ^gFrom conductometric measurements. ^hFrom potentiometric measurements. ⁱUsing only a 1:2 complexation model to fit the experimental data (M + 2L = ML₂), a value of 7.8 (6) for log*K* was calculated with a considerable increase of the sum of the squared errors in the fitting of the experimental data; a 1:1 + 1:2 complexation model is in agreement with conductometric measurement [38]. ¹A value of 19(1) was estimated by cyclic voltammetry for the cumulative formation constant (log β_2) of [Pb(L³)₂]²⁺ during the assisted transfer of Pb²⁺ at a polarised water/1,2-dichloroethane interface [46].



Fig. 8. (a) $[Pb(L^{1})][ClO_{4}]_{2}$ · $\frac{1}{2}H_{2}O$ in its dimeric form; (b) $[Pb(L^{2})][ClO_{4}]_{2}$ ·MeNO₂[38].



Fig. 9. (a) $[Pb(L^3)_2]^{2+}$, (b) $[Cd(L^3)][NO_3]_2$ [38].

complexes with Group VIII transition metal ions (see above). However, the ring cavity is not large enough to fully encapsulated larger d^{10} metal ions such as Cd²⁺ and Pb²⁺, which therefore are "perching" above the macrocyclic cavity of L¹-L³ (Figs. 8, 9) rather than "nesting" within it [38].

In $[Pb(L^1)][ClO_4]_2$ · $\frac{1}{2}H_2O$, two perchlorate ions and a water molecule bridge two symmetry related $[Pb(L^1)]^{2+}$ units to form a binuclear species (Fig. 8a). The structure of the complex cation $[Pb(L^3)_2]^{2+}$ (Fig. 9a) represents a rare example of a sandwich complex for Pb²⁺ with macrocyclic ligands and nicely supports the formation in solution of 1:2 M/L species

$$(M = Pb^{2+}, Cd^{2+}, Hg^{2+}; L = L^1 - L^3).$$

Copper(II), Silver(I)

Beside Pb^{2+} , Cd^{2+} , and Hg^{2+} , Cu^{2+} and Ag^+ are, from an analytical point of view, among the most targeted metal ions in industrial, medical and environmental samples. Their affinity for N/S-donor ligands stimulated our interest in their coordination chemistry towards L^1-L^7 .

The reaction of L^1-L^3 with Cu^{2+} was studied spectrophotometrically both in EtOH and in MeCN [47]. Immediately upon mixing the reactants, a blue-green colour is



Fig. 10. (a) Changes with time in the absorption spectrum of a solution of Cu^{2+} (4 × 10⁻⁴ M) in the presence of L^2 (1.6 × 10⁻³ M) in EtOH; (b) absorbance (at 370 nm)/molar ratio plots for EtOH solutions of Cu^{2+} (2 × 10⁻⁴) and L^1 (•), L^2 (•) or L^3 (•) immediately after mixing the reactants [47].

observed ($\lambda_{max} = 650$ nm). In time, this colour disappears and solutions turn to yellow ($\lambda_{max} = 450$ nm, Fig. 10a for L^2). This behaviour is observed for all three ligands in both in EtOH and in MeCN, and for solutions having different L/Cu^{2+} molar ratios (from 0.2 to 4). However, the blue-green colour persists for several hours if the L/Cu^{2+} molar ratio is lower than 1.

Fast spectrophotometric titrations of Cu^{2+} with the ligands in EtOH or MeCN by recording the spectra immediately after mixing the reactants (Fig. 10b) indicate a quantitative formation of $[Cu(L)]^{2+}$ ($L = L^{1-}L^{3}$) complexes. It is interesting to observe that further addition of the ligands beyond the 1:1

 L/Cu^{2+} molar ratio led to a gradual small decrease in absorbance at 650 nm, according to the observed instability of the species $[Cu(L)]^{2+}$ in the presence of excess ligands; this effect is particularly evident in the case of L^3 (see Fig. 10b). However, the transformation of the blue-green species $[Cu(L)]^{2+}$ into those responsible for the yellow colour is enough slow to allow both confirmation of their 1:1 stoichiometry by continuous variations plots under similar experimental conditions, and calculation of their formation constants (Table 2). It is important to point out at this stage that the calculated formation constants for the 1:1 complexes $[Cu(L)]^{2+}$ ($L = L^1-L^3$) are of the same order of magnitude and comparable with those calculated for the complexes of the same ligands with the metal ions Pb^{2+} , Cd^{2+} , and Hg^{2+} (Table 2). Furthermore, while in the case of Pb^{2+} a slight decrease in K_1 is observed on passing from L^1 to L^3 , a similar trend is not observed for Cu^{2+} and for the other metal ions considered (Table 2).

At the solid state, whatever the Cu²⁺/L molar ratio used (1:1 or 1:2), the reaction between $L^{1}-L^{3}$ and Cu(ClO₄)₂·2H₂O in EtOH/CH₂Cl₂ always resulted in solid products containing the 1:1 complexes, as demonstrated by elemental analysis, FAB mass spectrometry, and X-structural analysis for [Cu(L²)(ClO₄)]ClO₄ and [Cu(L³)(ClO₄)]ClO₄·¹/₂H₂O.

Several attempts were made to isolate 1:2 Cu^{2+}/L complexes at the solid state (presumably responsible for the yellow colour in solution which develops on either adding excess ligands to the metal or allowing 1:1 metal-to-ligand mixture to stand) using different starting copper(II) metal salts and solvents. Only from the reaction of L^1 with $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, and after addition of excess of NH_4PF_6 to the reaction mixture, was the complex [$\text{Cu}(\text{L}^1)_2$][PF_6]₂ separated as a red microcrystalline solid and unambiguously characterised by ESR to have a N_4 *pseudo*- tetrahedral coordination sphere around the metal centre [47]. In both structurally characterised complexes the ligands adopt a folded conformation typical for these types of macrocycles with the aliphatic chain of the



Fig. 11. (a) $[Cu(L^2)(ClO_4)]^+$; (b) $[Cu(L^3)(ClO_4)]^+$; (c) $[Cu(L^1)(Cl)(PPh_3)]$ [47].

ring tilted over the plane containing the phenanthroline unit (Fig. 11a, b). A pseudo-octahedral and a square-based pyramidal coordination spheres are reached at the metal centre in $[Cu(L^2)(ClO_4)]^+$ and $[Cu(L^3)(ClO_4)]^+$, respectively, by interaction of a perchlorate ion at the coordination site left free by the macrocycles. Quite remarkable is the structure of the Cu^I complex $[Cu(L^1)(Cl)(PPh_3)]$ (Fig. 11c) in which none of the S-donors in the aliphatic chain of the macrocycle is coordinated to the metal centre. A distorted tetrahedral coordination sphere at the Cu^I centre is reached *via* the two Ndonors of L¹, a chloride ligand and a PPh₃ unit. The metal ion is located under the plane of the phen moiety with the formation of a five- membered chelate ring showing a *pseudo*boat conformation [47].

The coordination chemistry in MeCN solution of Ag^+ was instead investigated towards L^1-L^3 , L^5 and L^6 by spectrofluorimetric, spectrophotometric, conductometric and potentiometric methods [39]. All techniques agreed on the formation in solution of only 1:1 [Ag(L)]⁺ complexes in the cases of L^1-L^3 (Figs. 12a, c). Formation of both 1:1 [Ag(L)]⁺ and 1:2 [Ag(L)₂]⁺ species were instead observed with L^5 and L^6 as clearly shown by the inflection points in the spectrofluorimetric and conductometric titration plots (Figs. 12b, d), and the compound [Ag(L^5)]BF₄ was also isolated at the solid state and structurally characterised [39].

Interestingly, the corresponding formation constants calculated from computer fitting to the proper models of the data obtained by all independent methods are in satisfactory agreement within experimental errors (Table 2). Furthermore, despite the different donor atom sets present in the five ligands considered, the calculated formation constants for the 1:1 $[Ag(L)]^+$ species are of the same order of magnitude and comparable to those calculated for Pb²⁺, Cd²⁺, Hg²⁺, and Cu²⁺, with the following decreasing order L² > L⁶ > L¹ > L³ > L⁵.

ANALYTICAL APPLICATIONS

"Molecular recognition" is a basic concept in "Supramolecular chemistry". When substrates are metal ions, the most obvious and common parameter to evaluate recognition is the thermodynamic stability (formation constant) of metal ion complexes and it mainly depends on the geometry of the ligand, the binding sites that it contains, the nature of the metal ion, and its stereoelectronic preferences. In the case of macrocyclic ligands, size complementarity between the metal ion and the ring cavity of the ligand is also an operational criterion to predict and evaluate preferential binding and recognition. The idea that on changing the nature of the binding sites (N, S rather than O) and their arrangement in the ligand can bring to the proper receptor for the target substrate with very high stability of "host-guest" interaction has been fundamental for the development of this field.

On these grounds, ligands $L^{1}-L^{3}$ cannot be considered selective receptors for the metal ions considered, in particular Pb²⁺, Cd²⁺, Hg²⁺, Cu²⁺, and Ag⁺ (see Table 2), and their use as molecular fluorescent chemosensor for these ions is strongly



Macrocycles Containing the 1,10-Phenanthroline Sub-unit

Fig. 12. Fluorescence intensity/molar ratio plots for (a) $\mathbf{L}^1(\bullet)$, $\mathbf{L}^2(\bullet)$, and $\mathbf{L}^3(\blacktriangle)$; (b) $\mathbf{L}^5(\bullet)$ and $\mathbf{L}^6(\bigstar)$ (2.0× 10^{-5} -4.5 × 10^{-5} M, MeCN, 25 °C) in the presence of increasing amounts of Ag⁺. Inset to (b): enlargement of the fluorescence intensity/molar ratio plot for the titration of \mathbf{L}^5 with Ag⁺. Molar conductance/molar ratio plots for a solution of Ag⁺ (<1.0 × 10^{-5} M, MeCN, 25 °C) in the presence of increasing amounts of C L¹ (•), $\mathbf{L}^2(\bullet)$, and $\mathbf{L}^3(\blacktriangle)$; (d) $\mathbf{L}^5(\bullet)$ and $\mathbf{L}^6(\bigstar)$ [39].

jeopardized. However, in some cases a different effect on the fluorescent emission of the heteroaromatic moiety of L^1-L^3 has been observed upon interaction with the various metal ions,

and this certainly represents a great spur to continue the work by properly changing the structure of these ligands so to reach selectivity of metal ion complexation and to improve the



Fig. 13. Schematic of a PVC-membrane ions-selective electrode.

sensor performance.

It should not be forgotten that efficiency and selectivity of the "host-guest" interaction are strongly determined also by the medium in which it takes place. This prompted us to study the coordination properties of $L^{1}-L^{3}$ when incorporated into organic membranes and involved in transport processes. In particular, we wanted to test the potentiality of these ligands as selective neutral carriers in the preparation of potentiometric sensors, in particular ion-selective PVC-membrane electrodes.

Ion-Selective Electrodes (ISEs)

Usually, a PVC-membrane ion selective electrode device with internal reference solution (CONISE) can be represented by Fig. 13 [4,6]. The neutral macrocyclic ionophore is dispersed into a heterogeneous, quasi-liquid membrane composed of PVC (inert matrix), a plasticizer (solvent), and other additives such as lipophilic anions. Some firms manufacture potentiometric sensors combining the ISE with the reference electrode (combined ISEs). The response of an ISE is related to the activity (concentration) of a sensed ion in the aqueous tested solution, and originates from the process of charge separation generating a double electric layer at the tested solution/membrane interface. This process is determined by a selective interaction between the neutral carrier in the membrane surface layer and the ions in the diffusion layer of the tested solution. The potential drop at the solution/membrane interface and, therefore, the selectivity of the device depends on transport processes and ability of the carrier to reversibly bind hydrophilic ions into complexes which are readily soluble/transported into the membrane hydrophobic phase, which are strongly determined by the membrane composition and lipophilicity/mobility of the carrier-substrate system.

The most important characteristic of any ISE is its relative response for the target ion over other ions present in solution, which is expressed in terms of potentiometric selectivity coefficients $K^{Pot}{}_{M,M}$, describing the preference by the membrane for an interfering ion M^{n+} relative to the primary ion M^{m+} . $K^{Pot}{}_{M,M}$ can be determined from potential measurements of solutions containing a fixed amount of M^{m+} and varying amounts of the interfering ion M^{n+} according to the equation (2):

$$K^{\text{Pot}}_{M',M} a^{m/n}_{M'} = a_{M'} \{ \exp[(E_2 - E_1)(F/RT)] \} - a_{M'}$$
(2)

where E_1 and E_2 are the electrode potentials for the solutions

Macrocycles Containing the 1,10-Phenanthroline Sub-unit



Fig. 14. Potential response of various PVC-membrane electrodes based on (a) L^{1} [48]; (b) L^{3} [54]; (c) L^{5} [55].

of M^{m+} ion alone and for the solutions containing M^{m+} and interfering M^{n+} ions, respectively. The lower the $K^{Pot}_{M',M}$, the higher the selectivity of the ISE device for the primary ion M^{m+} .

In preliminary experiments, L¹ was tested as neutral carrier in PVC-membrane CONISE for a wide range of metal ions (Fig. 14a) [48]. Only the Cu^{2+} electrode exhibited an excellent Nernstian behaviour over a wide concentration range. CONISEs with the same membrane composition but containing L^2 or L^3 revealed the order $L^1 > L^2 > L^3$ in the efficiency of these ligands as Cu²⁺ carriers. The optimal membrane composition resulted to have a PVC:BA (benzyl acetate):L¹:OA (oleic acid) percentage ratio of 32:54:6:8 to which corresponded a Nerstian behaviour [29.4(5) mV decade⁻¹ slope] of the prepared CONISE (internal reference solution 1.0×10^{-3} M Cu(NO₃)₂) in a pH range of 2.5-5.5 for the tested solution, over a Cu^{2+} concentration range of 1.0 × $10^{-5} - 2.0 \times 10^{-1}$ M with a limit of detection (LOD) of 8.6 × 10^{-6} M (0.5 ppm). The selectivity coefficients for some common interfering ions of this Cu²⁺-selective CONISE based on L^1 are compared in Table 3 with the corresponding

coefficients reported for some PVC-membrane Cu^{2+} -selective CONISEs based on different neutral cyclic and acyclic ion carriers [48-53]. Quite interesting are the low values of the selectivity coefficients for the interfering ions Ag⁺, Pb²⁺, Cd²⁺, and Hg²⁺ which showed formation constants of the corresponding 1:1 complexes with L¹ comparable to that for the [Cu(L¹)]²⁺ species (Table 2).

In this respect, it was quite surprising to discover an high efficiency and selectivity of L^3 over L^1 and L^2 in the preparation of a PVC-membrane Ag⁺-selective CONISE (Fig. 14b) [54]. In fact, from the formation constants of $[Ag(L)]^+$ species reported in Table 2, L^3 shows the lowest affinity to Ag⁺, compared to L^1 and L^2 . This once again demonstrates the importance of transport dynamics, beside structural features of the carrier, in determining the potentiometric selectivity of ISEs, which can even follow a trend opposite to that indicated by thermodynamic studies. As a further example, L^5 (Fig. 14c) and L^6 both showed an ability and selectivity comparable to that of L^3 as neutral carrier in the preparation of PVC-membrane Ag⁺-selectice CONISEs [55], despite their different affinity to Ag⁺ in MeCN solutions (Table 2). Using a

Carriers	LOD	Ag ⁺	Tl ⁺	Hg ²⁺	Cd ²⁺	Pb ²⁺	Ni ²⁺	Zn ²⁺	Sr ²⁺	Ref.
	3.2×10^{-7}				-2.7		-3.3	-2.0		[49]
$ \begin{array}{c} $	3.2×10^{-7}				-4.4	-0.7	-3.2	-2.3	-3.6	[50]
	1.2×10^{-5}			-2.4	-1.6	-2.2	-2.0	-2.3	-1.0	[51]
N N N N N N N N N N N N N N N N N N N	3.1 × 10 ⁻⁶	-0.1	-2.5	-2.0	-2.7	-2.7	-3.0	-3.0		[52]
	5.0×10^{-6}			-1.2	-2.1	-2.4	-1.5	-2.1	-3.1	[53]
L^1	8.0×10^{-6}	-2.1	-2.9	-3.1	-3.4	-2.7	-3.2	-2.9	-2.8	[48]

Table 3. Limit of Detection (LOD) and Selectivity Coefficients (logK^{Pot}) of Different Copper(II) Ion-Selective Electrodes

membrane with a PVC:NPOE (o-nitrophenyloctyl ether): L³:OA (oleic acid) percentage ratio of 32:54:6:8 a Nernstian behaviour (59.4 mV decade⁻¹ slope) of the prepared CONISE (internal reference solution 1.0×10^{-3} M AgNO₃) in a pH range of 3.0-8.0 for the tested solution was observed over a Ag⁺ concentration range of 1.0×10^{-5} - 1.0×10^{-1} M with a limit of detection of 8.0×10^{-6} M. Performances could drastically be improved by supporting the membrane solution with the optimal composition on a graphite rod and using a solid contact electrode (SCISE) (Nernstian behaviour range $5.0 \times$ $10^{-8} - 4.0 \times 10^{-2}$ with a limit of detection of 3.0×10^{-8}) [54]. For L^5 and L^6 the optimal membrane compositions for the corresponding prepared CONISEs (internal reference solution 1.0×10^{-3} M AgNO₃) were PVC/NPOE/L⁵/OA = 30/56/6/8 $PVC/NPOE/L^{6}/OA = 30/55/7/8$ percentage ratios, and

concentration ranges 1.0×10^{-5} - 1.0×10^{-1} M (LOD 8.0×10^{-6} M) and 1.0×10^{-6} - 1.0×10^{-1} M (LOD 8.0×10^{-7} M) for L⁵ and L⁶, respectively. Once again, performances could drastically be improved by supporting the membrane solutions with the optimal compositions on a graphite rod and using a solid contact electrode (SCISE) (Nernstian behaviour range 5.0×10^{-8} - 5.0×10^{-2} , LOD 2.0×10^{-8} for L⁵, and 3.0×10^{-8} - 5.0×10^{-2} , LOD 1.0×10^{-8} for L⁶ [55]. In Table 4 the selectivity coefficients of different Ag⁺-selective CONISEs for some common interfering ions are reported and compared to those found for the CONISEs and SCISEs based on L³, L⁵, and L⁶ [11,56-59]. In particular a high selectivity is observed for Ag⁺ over the Pb²⁺, Hg²⁺, Cd²⁺, and Cu²⁺ ions.

respectively. A Nernstian behaviour was observed in the pH

range of 3.0-7.0 for the tested solutions over Ag⁺

Carriers	LOD	Na ⁺	Tl ⁺	Ca ²⁺	Co ²⁺	Ni ²⁺	Cu ²⁺	Zn ²⁺	Cd ²⁺	Pb ²⁺	Hg ²⁺	Ref.
	6.3×10^{-7}	-3.7		-5.2	-5.2	-5.1	-5.1		-4.9	-5.3	-39	[56]
S S S	8.0×10^{-7}	-4.1		-3.8	-4.4	-3.9	-3-3		-3.1	-3.0	-3.0	[57]
$ \begin{array}{c} S & S \\ \parallel & \parallel \\ EtO & S & S & P \\ OEt & OEt & OEt \end{array} $	6.0×10^{-7}	-4.7		-4.8		-4.9	-2.9	-4.0	-3.5	-3.0		[58]
	4.0×10^{-6}	-1.4	-0.2	-1.8	-1.8	-2.0	-2.4	-1.6	-1.6	-1.0	-2.2	[11]
+ + of off 2 c=o ON	5.0×10^{-6}	-4.3		-4.5		-3.9	-4.4	-4.4	-4.4	-3.8	-1.2	[59]
L^3_2 CONISE	8.0×10^{-6}	-3.6	-1.6	-4.0	-2.2	-3.1	-1.4	-2.9	-3.0	-2.5	-2.3	[54]
L' SCISE	3.0×10^{-8}	-4.1	-2.8	-4.5	-3.4	-3.4	-2.9	-3.4	-3.6	-2.9	-3.1	[54]
L' SCISE	2.0×10^{-6}	-4.2	-2.6	-4.7			-2.6		-3.5	-2.8	-3.2	[55]
L° SCISE	1.0×10^{-6}	-4.3	-3.1	-5.1			-2.9		-3.6	-2.8	-3.3	55

Table 4. Limit of Detection (LOD) and Selectivity Coefficients ($\log K^{Pot}$) of Different Silver(I) Ion-selective Electrodes

Although the coordination chemistry of \mathbf{L}^7 containing two heteroaromatic sub-units towards any kind of metal ions has not been explored yet, preliminary studies on the fluorescence emission variation for this macrocyclic ligand upon addition of increasing amounts of lanthanide ions showed a marked selectivity towards Nd³⁺ over Yb³⁺, Gd³⁺, Sm³⁺, and La³⁺ with formation of both $[\mathbf{M}(\mathbf{L}^7)]^{3+}$ and $[\mathbf{M}(\mathbf{L}^7)_2]^{3+}$ species (Fig. 15a) [37]. On these grounds, \mathbf{L}^7 was tested as neutral carrier in PVC-membrane CONISE for a wide range of metal ions (Fig. 15b) [37]. Only the Nd³⁺ electrode exhibited an excellent sensitive response with a Nernstian behaviour over a wide Nd³⁺ concentration range. Using a membrane solution with a PVC/NPOE/L⁷/OA percentage ratio composition of 30/50/16/4 it was possible to prepare the first highly Nd³⁺-selective CONISE (internal reference solution 1.0×10^{-3} M Nd(NO₃)₃) with a Nernstian behaviour [20.0(2) mV decade⁻¹ slope] in a pH range of 4.0-6.5 for the tested solution, over a Nd³⁺ concentration range of 1.0×10^{-6} - 1.0×10^{-2} M with a limit of detection of 7.9×10^{-7} M.

Separation Procedures

In last twenty years, supported liquid membranes (SLMs)



Fig. 15. (a) Fluorescence intensity-molar ratio plots for a 9.0 × 10⁻⁶ M L⁷ in MeCN at 25.0 °C in the presence of increasing amounts of La³⁺, Sm³⁺, Gd³⁺, Yb³⁺ and Nd³⁺ ions; (b) potential response of various PVC-membrane electrodes based on L⁷ [37].

have received increasing attention as alternatives to liquidliquid extraction and other separation techniques for the selective removal of ions or neutral molecules from dilute solutions [60-63]. In view of the simplicity of operation, economical utilization of the extractant and lack of solvent entrainment, SLMs are more advantageous than conventional solvent extraction processes. The supported liquid membrane enrichment technique involves the use of a thin impregnated microporous membrane, separating feed (source phase) and strip (receiving phase) solutions. Several different membrane supports have been used to make SLMs. These include PP, PVDF, PTFE, silicones etc. [64-67]. The requirement for a good polymeric support are high porosity, small pore size, good mechanical strength, chemical resistance, thinness, hydrophobicity and low cost. The membrane is impregnated with a water-immiscible solvent containing a suitable lipophilic ligand as ion carrier and then placed between the feed and strip aqueous compartments. The choice of the appropriate counter anions in the feeding and stripping solutions and the concentration of the neutral carrier in the supported membraneare particularly important in determining the efficiency and selectivity of the transport process of the target metal ion.

On the basis of the results obtained in the preparation of Ag^+ -selectice ISEs (see above), the ligands $L^{1}-L^{3}$ were tested as neutral carriers in the preparation of SLMs for the selective transport of Ag^+ . Surprisingly the most efficient ligand resulted to be L^2 in a 0.01 M concentration in a NPOE membrane [68]. This result better agree with the decreasing order $L^2 > L^1 > L^3$ of the calculated formation constant for the 1:1 $[Ag(L)]^+$ species in MeCN solution (Table 2), and strongly support the importance of the experimental conditions in which a macrocyclic ligand performs the coordination process. Maximum transport, nearly 90% in three hours time, was

observed in the presence of 0.01 M picric acid in the feeding solution with a [picric acid]/[Ag⁺] ratio of about 100, and 0.03 M thiosulfate ion as scavenger for the transported Ag⁺ in the stripping solution. Transport experiments were made with Mg²⁺, Ca²⁺, Sr²⁺, Ba²⁺, Co²⁺, Ni²⁺, Zn²⁺, Cu²⁺, Cd²⁺, Pb²⁺, and Hg²⁺ present initially at [M²⁺]/[Ag⁺] \geq 5 in the feed solution. None of these metal ions used interfere the transport of silver ion through the SLM system, even at such high [M²⁺]/[Ag⁺] ratios up to 100. It is interesting to point out that, despite their well-known advantages, the SLMs suffer from instability with time. This is mainly due to loss of carrier and/or membrane solvent from the membrane phase, thus influencing both flux and selectivity of the membrane. The Ag⁺-selective SLM based on L² was found to be quite stable for at least 48 hours without loss of efficiency over re-use in this period of time.

Ligands L^1-L^3 were also tested as sequestering agents for selective solid phase extraction and determination of trace level of Ag^+ ion [69]. In particular, L^1-L^3 (5 mg) were supported onto octadecyl silica membrane disks and 25-2000 ml of sample solutions in the pH range 3.5-8.0 containing 10 μg of Ag⁺ were passed through the membranes at a flow rate of 20 ml min⁻¹. The retained Ag⁺ ions were then stripped from the disk with a minimal amount of 2.0 M thiosulfate solution as eluent and subsequently measured by atomic absorption spectrometry. A quantitative and selective absorption of Ag⁺ was only possible again with L^3 . The retention of other cations such as Pb²⁺, Cd²⁺, Hg²⁺, and Cu²⁺ was quite low and all of them could be separated completely from the Ag⁺ ion. The maximum capacity of the membrane modified with 5 mg of L^3 was evaluated to be 917 \pm 15 µg of Ag⁺ on the disk. The proposed method permitted large enrichment factors of 200 and higher. The limit of detection found to be 100 ng silver ion per 100 ml.

CONCLUSIONS

Beside the intrinsic interest that the coordination chemistry of the ligands here discussed might arise in the reader, in our opinion, the message to-take-home from the results here summarised is that the ability of macrocyclic ligands to behave as selective molecular sensors or ionophores for target guest species is not only determined by the affinity for these in terms of formation constants of the corresponding complexes, but also by the way and the medium in which the host-guest interaction takes place. L^{1} - L^{3} are not selective and specific fluorescent molecular sensors for the metal ions studied, nevertheless they become selective ionophores once incorporated into organic membranes and can be used for the construction of selective potentiometric sensors. Many times macrocycle-based molecular systems do not accomplish properly to the role of specific molecular sensors for which they have been designed in the first place. A good practise (not always considered) should be, therefore, to test their ability as receptors in molecular recognition processes in different chemical situations and for different purposes.

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