

# Interaction of Mixed-Donor Macrocycles Containing the 1,10-Phenanthroline Subunit with Selected Transition and Post-Transition Metal Ions: Metal Ion Recognition in Competitive Liquid–Liquid Solvent Extraction of Cu<sup>II</sup>, Zn<sup>II</sup>, Pb<sup>II</sup>, Cd<sup>II</sup>, Ag<sup>I</sup>, and Hg<sup>II</sup>

M. Carla Aragoni,<sup>†</sup> Massimiliano Arca,<sup>†</sup> Andrea Bencini,<sup>‡</sup> Silvia Biagini,<sup>‡</sup> Alexander J. Blake,<sup>§</sup> Claudia Caltagirone,<sup>†</sup> Francesco Demartin,<sup>||</sup> Greta De Filippo,<sup>†</sup> Francesco A. Devillanova,<sup>†</sup> Alessandra Garau,<sup>†</sup> Karsten Gloe,<sup>⊥</sup> Francesco Isaia,<sup>†</sup> Vito Lippolis,<sup>\*,†</sup> Barbara Valtancoli,<sup>‡</sup> and Marco Wenzel<sup>⊥</sup>

*Dipartimento di Chimica Inorganica ed Analitica, Università degli Studi di Cagliari, S.S. 554 Bivio per Sestu, 09042 Monserrato (CA), Italy, Dipartimento di Chimica, Università degli Studi di Firenze, Via della Lastruccia 3, 50019 Sesto Fiorentino, Firenze, Italy, School of Chemistry, The University of Nottingham, University Park, NG7 2RD Nottingham, U.K., Dipartimento di Chimica Strutturale e Stereochimica Inorganica, Università di Milano, Via G. Venezian 21, 20133 Milano, Italy, and TU Dresden, Department of Chemistry, D-01062 Dresden, Germany*

Received March 27, 2008

Two new mixed aza-thia crowns 5-aza-2,8-dithia[9]-(2,9)-1,10-phenanthrolinephane (**L**<sup>4</sup>) and 2,8-diaza-5-thia[9]-(2,9)-1,10-phenanthrolinephane (**L**<sup>7</sup>) have been synthesized and characterized. The coordination behavior of **L**<sup>4</sup> and **L**<sup>7</sup> toward the metal ions Cu<sup>II</sup>, Zn<sup>II</sup>, Pb<sup>II</sup>, Cd<sup>II</sup>, Hg<sup>II</sup>, and Ag<sup>I</sup> was studied in aqueous solution by potentiometric methods, in CD<sub>3</sub>CN/D<sub>2</sub>O 4:1 (v/v) by <sup>1</sup>H NMR titrations and in the solid state. The data obtained were compared with those available for the coordination behavior toward the same metal ions of structurally analogous mixed donor macrocyclic ligands **L**<sup>1</sup>–**L**<sup>3</sup>, **L**<sup>5</sup>, **L**<sup>6</sup>: all these contain a phenanthroline subunit but have only S/O/N(aromatic) donor groups in the remaining portion of the ring and are, therefore, less water-soluble than **L**<sup>4</sup> and **L**<sup>7</sup>. The complexes [Cd(NO<sub>3</sub>)<sub>2</sub>(**L**<sup>5</sup>)], [Pb(**L**<sup>7</sup>)](ClO<sub>4</sub>)<sub>2</sub> · 1/2 MeCN, [Pb(**L**<sup>4</sup>)](ClO<sub>4</sub>)<sub>2</sub> · MeCN, and [Cu(**L**<sup>7</sup>)](ClO<sub>4</sub>)<sub>2</sub> · 3/2 MeNO<sub>2</sub> were characterized by X-ray crystallography. The efficacy of **L**<sup>1</sup>–**L**<sup>7</sup> in competitive liquid–liquid metal ion extraction of Cu<sup>II</sup>, Zn<sup>II</sup>, Cd<sup>II</sup>, Pb<sup>II</sup>, Ag<sup>I</sup>, and Hg<sup>II</sup> was assessed. In the absence of Hg<sup>II</sup>, a clear extraction selectivity for Ag<sup>I</sup> was observed in all systems investigated.

## Introduction

Following the pioneering work of the 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 for a wide variety of fields: the development of some fundamental aspects of “Supramolecular Chemistry” such as “molecular recognition”, “host-guest interactions”, and the design of sensors and smart artificial “molecular devices” is intimately

linked to the study of macrocyclic chemistry.<sup>1–4</sup> Increasingly sophisticated macrocyclic systems differing in molecular shape, architecture, flexibility, arrangement of structural groups, binding sites, and reactive functions continue to be designed and synthesized with the aim of achieving control over the strength, selectivity, and dynamics of the binding processes between the macrocyclic ligands and a variety of cationic, anionic, neutral, organic, and inorganic substrates.

\* To whom correspondence should be addressed. E-mail: lippolis@unica.it. Phone: +39 0706754467. Fax: +39 0706754456.

<sup>†</sup> Università degli Studi di Cagliari.

<sup>‡</sup> Università degli Studi di Firenze.

<sup>§</sup> The University of Nottingham.

<sup>||</sup> Università di Milano.

<sup>⊥</sup> TU Dresden.

(1) *Macrocyclic Chemistry, Current Trends and Future Perspectives*; Gloe, K., Ed.; Springer: New York, 2005; ISBN 1–4020–3364–8.

(2) *Coord. Chem. Rev.* **1996**, *148*, 2001, 222; and **2000**, 205; Theme Issue: “Macrocyclic Chemistry”, “Metallosupramolecular Chemistry”, and “Luminescent Sensors” respectively.

(3) *Molecular Devices and Machines, A Journey into the Nanoworld*; Balzani, V., Credi, A., Venturi, M., Eds.; Wiley-VCH: Weinheim, 2003; ISBN 3–527–30506–8.

(4) *J. Mat. Chem.* **2005**, *15*; Theme Issue: “Fluorescent Sensors”.

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 science,<sup>5</sup> and many macrocyclic systems have been employed as selective extractants/ionophores for transition and post-transition metal ions in a range of solvent extraction and bulk membrane transport studies.

When the substrates are metal ions, the most obvious and common parameter to evaluate recognition is the thermodynamic stability (formation constant) of metal ion complexes: this parameter mainly depends on the geometry of the ligand, the binding sites that it contains, and on the nature and stereoelectronic preferences of the metal ion. 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. One consideration has been fundamental to the development of macrocyclic chemistry: it is possible to confer on the appropriate macrocyclic ligand the potential for a very high degree of "host-guest" interaction

with the target substrate, either by changing the "hard-soft" nature and disposition of the binding sites or by modifying the flexibility of the macrocycle.

For example, because of the specific complexing abilities of crown ethers toward hard Group I and II metal ions, these ligands have been used as neutral carriers for the construction of PVC-based ion selective electrodes (ISEs) for alkali and alkaline earth metal cations and for performing selective separations.<sup>5-7</sup> On the other hand, thioether macrocycles have come to great prominence in the past decade because of their selective coordination properties toward soft transition metal ions, and coinage metals in particular,<sup>8,9</sup> and numerous analytical applications have appeared.<sup>5,10-13</sup> In between these two classes of compounds, many mixed-donor host macrocyclic chemical structures, also featuring rigid subunits in the chelating ring, have been designed and synthesized for a variety of guest compounds, and successfully used for analytical, sensing and separation purposes.<sup>1-5,14-38</sup>

In this context we have been engaged for the past decade in the development of a new class of mixed N/O/S-donor macrocycles featuring a phenanthroline (phen) subunit as an integral part of the macrocyclic structure (Figure 1). Our initial aim was to combine the physicochemical and coordinating properties of phen with those of aliphatic thioether crowns and to test the potential of these cyclic phenanthroline derivatives as efficient complexing agents and selective extractants for environmental and industrial important "soft" metal ions and as fluorescent sensors for their detection in solution. In previous papers we reported on the coordination chemistry of this type of macrocycles toward Ni<sup>II</sup>, Pd<sup>II</sup>, Pt<sup>II</sup>, Rh<sup>III</sup>, Ru<sup>II</sup> (L<sup>1</sup>, L<sup>2</sup>),<sup>39-41</sup> Pb<sup>II</sup>, Cd<sup>II</sup>, Hg<sup>II</sup>, Cu<sup>II</sup> (L<sup>1</sup>-L<sup>3</sup>),<sup>42-44</sup> and Ag<sup>I</sup> (L<sup>1</sup>-L<sup>3</sup>, L<sup>5</sup>)<sup>45</sup> in solution (MeCN, EtOH) and/or in the solid state. We documented the ability of these macro-

- (5) *Macrocyclic Compounds in Analytical Chemistry*; Zolotov, Y. A., Ed.; Wiley & Sons: New York, 1997; ISBN 0-471-17262-6.
- (6) Izatt, R. M.; Clark, G. A.; Bradshaw, J. S.; Lamb, J. D.; Christensen, J. J. *Sep. Purif. Methods* **1986**, *15*, 21.
- (7) Bühlmann, P.; Pretsch, E.; Bakker, E. *Chem. Rev.* **1998**, *98*, 1593.
- (8) Blake, A. J.; Schröder, M. *Adv. Inorg. Chem.* **1990**, *35*, 1.
- (9) Reid, G.; Schröder, M. *Chem. Soc., Rev.* **1990**, *19*, 239.
- (10) Saito, K.; Taninaka, I.; Muratami, S.; Muramatsu, A. *Talanta* **1998**, *46*, 1187.
- (11) Shamsipur, M.; Mashhadizadeh, M. H. *Sep. Purif. Technol.* **2000**, *20*, 147.
- (12) Mashhadizadeh, M. H.; Shamsipur, M. *Anal. Chim. Acta* **1999**, *381*, 111.
- (13) Gupta, V. K.; Jain, S.; Khurana, U. *Electroanalysis* **1997**, *9*, 478.
- (14) *The Chemistry of Macrocyclic Ligands Complexes*; Lindoy, L. F., Ed.; Cambridge University Press: New York, 1986; ISBN 0-521-25261-X.
- (15) Casabò, J.; Teixidor, F.; Escriche, L.; Viqas, C.; Pérez-Jiménez, C. *Adv. Mater.* **1995**, *7*, 238.
- (16) Tamayo, A.; Lodeiro, C.; Escriche, L.; Casabò, J.; Covelo, B.; Gonzalez, P. *Inorg. Chem.* **2005**, *44*, 8105.
- (17) Blake, A. J.; Bencini, A.; Caltagirone, C.; De Filippo, G.; Dolci, L. S.; Garau, A.; Isaia, F.; Lippolis, V.; Mariani, P.; Prodi, L.; Montalti, M.; Zaccaroni, N.; Wilson, C. *Dalton Trans.* **2004**, 2771.
- (18) Shamsipur, M.; Poursaberi, T.; Rezapour, M.; Ganjali, M. R.; Mousavi, M. F.; Lippolis, V.; Montesu, D. R. *Electroanal.* **2004**, *16*, 1336.
- (19) Shamsipur, M.; Hosseini, M.; Alizadeh, K.; Alizadeh, N.; Yari, A.; Caltagirone, C.; Lippolis, V. *Anal. Chim. Acta* **2005**, *533*, 17.
- (20) Ishikawa, J.; Sakamoto, H.; Mizuno, T.; Otomo, M. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 3071.
- (21) Masuda, Y.; Zhang, Y.; Yan, C.; Li, B. *Talanta* **1998**, *46*, 203.
- (22) Siswanta, D.; Nagtsuka, K.; Yamada, H.; Kumakura, K.; Hisamoto, H.; Sichi, K.; Toshima, K.; Suzuki, K. *Anal. Chem.* **1996**, *68*, 4166.
- (23) Casabò, J.; Escriche, L.; Alegret, S.; Jaime, C.; Pérez-Jiménez, C.; Mestres, L.; Rijs, J.; Molins, E.; Miravittles, C.; Teixidor, F. *Inorg. Chem.* **1991**, *30*, 1893.
- (24) Chandler, C. J.; Deady, L. W.; Reiss, J. A. *J. Heterocyclic Chem.* **1986**, *23*, 1327.
- (25) Sugihara, H.; Hiratani, K. *Coord. Chem. Rev.* **1996**, *148*, 285.
- (26) Bazzicalupi, C.; Bencini, A.; Fusi, V.; Giorgi, C.; Paoletti, P.; Valtancoli, B. *Inorg. Chem.* **1998**, *37*, 941.
- (27) Bencini, A.; Bernardo, M. A.; Bianchi, A.; Fusi, V.; Giorgi, C.; Pina, F.; Valtancoli, B. *Eur. J. Inorg. Chem.* **1999**, *11*, 1911.
- (28) Bang, K. S.; Nielsen, M. B.; Zubarev, R.; Becher, J. *Chem. Commun.* **2000**, 215.
- (29) Bencini, A.; Bianchi, A.; Giorgi, C.; Fusi, V.; Masotti, A.; Paoletti, P. *J. Org. Chem.* **2000**, *65*, 7686.
- (30) Bencini, A.; Bianchi, A.; Giorgi, C.; Valtancoli, B. *J. Inclusion Phenom.* **2001**, *41*, 87.
- (31) Pugliesi, A.; Tenaglia, M.; Annunziata, R.; Bologna, A. *Tetrahedron Lett.* **2003**, *44*, 2947.
- (32) Bencini, A.; Berni, E.; Bianchi, A.; Fornasari, P.; Giorgi, C.; Lima, J. C.; Lodeiro, C.; Melo, M. J.; de Melo, J. S.; Parola, A. J.; Pina, F.; Pina, J.; Valtancoli, B. *Dalton Trans.* **2004**, 1934.
- (33) Bencini, A.; Bianchi, A.; Lodeiro, C.; Masotti, A.; Parola, A. J.; Pina, F.; de Melo, J. S.; Valtancoli, B. *Chem. Commun.* **2000**, 1639.
- (34) Bazzicalupi, C.; Bencini, A.; Bianchi, A.; Giorgi, C.; Fusi, V.; Masotti, A.; Valtancoli, B.; Roque, A.; Pina, F. *Chem. Commun.* **2000**, 561.
- (35) Glenney, M. W.; Lacombe, M.; Love, J. B.; Blake, A. J.; Lindoy, L. F.; Luckay, R. C.; Gloe, K.; Antoniolli, B.; Wilson, C.; Schröder, M. *New J. Chem.* **2006**, *12*, 1755.
- (36) Vasilescu, I. M.; Bray, D. J.; Clegg, J. K.; Lindoy, L. F.; Meehan, G. V.; Wei, G. *Dalton Trans.* **2006**, 5115.
- (37) Price, J. R.; Fainerman-Melnikova, M.; Fenton, R. R.; Gloe, K.; Lindoy, L. F.; Rambusch, T.; Skelton, B. W.; Turner, P.; White, A. H.; Wichmann, K. *Dalton Trans.* **2004**, 3715.
- (38) Gasperov, V.; Galbraith, S. G.; Lindoy, L. F.; Rumbel, B. R.; Skelton, B. W.; Tasker, P. A.; White, A. H. *Dalton Trans.* **2005**, 139.
- (39) Arca, M.; Blake, A. J.; Casabò, J.; Demartin, F.; Devillanova, F. A.; Garau, A.; Isaia, F.; Lippolis, V.; Kivekas, R.; Muns, V.; Schröder, M.; Verani, G. *J. Chem. Soc., Dalton Trans.* **2001**, 1180; and refs therein.
- (40) Blake, A. J.; Devillanova, F. A.; Garau, A.; Harrison, A.; Isaia, F.; Lippolis, V.; Tiwary, S. K.; Schröder, M.; Verani, G.; Whittaker, G. *J. Chem. Soc., Dalton Trans.* **2002**, 4389; and refs therein.
- (41) Blake, A. J.; Caçote, M. H. M.; Devillanova, F. A.; Garau, A.; Isaia, F.; Lippolis, V.; Pereira, C. M.; Silva, F.; Tei, L. *Eur. J. Inorg. Chem.* **2002**, 1816.
- (42) Aragoni, M. C.; Arca, M.; Demartin, F.; Devillanova, F. A.; Isaia, F.; Garau, A.; Lippolis, V.; Jalali, F.; Papke, U.; Shamsipur, M.; Tei, L.; Yari, A.; Verani, G. *Inorg. Chem.* **2002**, *41*, 6623.
- (43) Ferreira, E. S.; Garau, A.; Lippolis, V.; Pereira, C. M.; Silva, F. *J. Electroanal. Chem.* **2006**, *587*, 155.

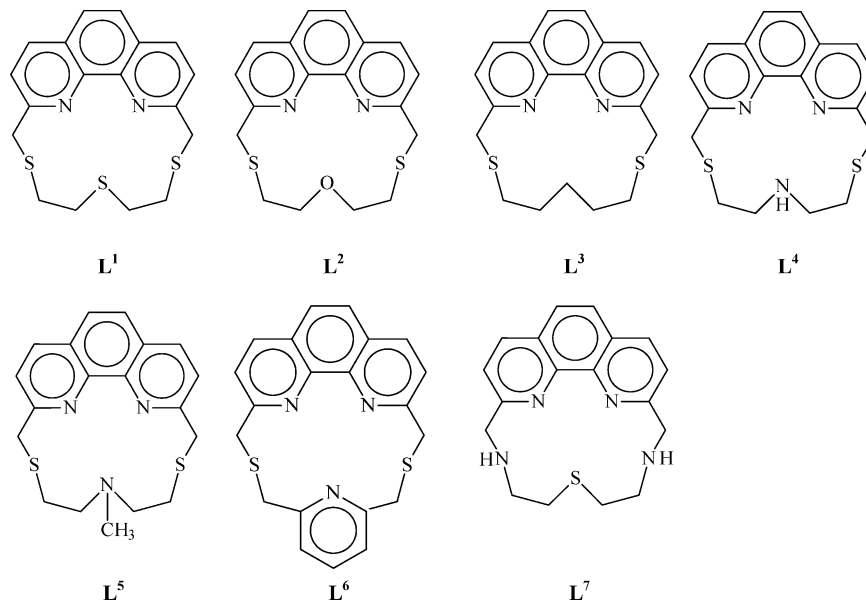


Figure 1. Summary of Ligands.

cyclic ligands to behave as selective ionophores for target guest metal ion species, which is strongly determined by the medium in which the “host-guest” interaction takes place (solution or bulky organic membranes).

For example, solution studies in MeCN demonstrated the inability of these ligands (in particular  $L^1$ – $L^3$ ) to work as selective and specific fluorescent chemosensors for heavy transition and post-transition metal ions ( $Pb^{II}$ ,  $Cd^{II}$ ,  $Hg^{II}$ ),<sup>42</sup> and the formation constants evaluated for the 1:1 complexes between  $L^1$ – $L^3$ ,  $L^5$  and  $Pb^{II}$ ,  $Cd^{II}$ ,  $Hg^{II}$ ,  $Cu^{II}$ , and  $Ag^I$  in MeCN are of the same order of magnitude.<sup>42–45</sup> Nevertheless, and despite the undifferentiated affinity of these ligands for the metal ions considered, some of them are extremely sensitive to the presence of  $Cu^{II}$  ( $L^1$ )<sup>46</sup> or  $Ag^I$  ( $L^2$ ,  $L^3$ ,  $L^5$ )<sup>47–51</sup> in the presence of other metal ions in transport processes across organic membranes. For example,  $L^1$  and  $L^3$  have been successfully used as neutral ionophores in the construction of PVC-based ion-selective electrodes (ISEs) for analytical detection and separation of  $Cu^{II}$  and  $Ag^I$ , respectively. Following these studies, here we report the synthesis and the coordination properties toward  $Cu^{II}$ ,  $Zn^{II}$ ,  $Cd^{II}$ ,  $Pb^{II}$ ,  $Hg^{II}$ , and  $Ag^I$  in aqueous solution and in the solid state of two new members of this family of macrocyclic ligands, namely  $L^4$  and  $L^7$ , both characterized by secondary amino groups

in the aliphatic portion of the ring. These two ligands have been synthesized to expand the family of homologous macrocycles made by us to include more hydrophilic members. We also set out to compare all of them as ionophores for metal ions using a liquid–liquid extraction technique which has not previously been applied to this kind of macrocycles. Indeed, we report here on the efficacy of  $L^1$ – $L^7$  in experiments involving competitive liquid–liquid solvent extraction of  $Cu^{II}$ ,  $Zn^{II}$ ,  $Pb^{II}$ ,  $Cd^{II}$ ,  $Hg^{II}$ , and  $Ag^I$  which were performed for  $Zn^{II}$  and  $Ag^I$  using a radiotracer technique.

## Experimental Section

All melting points are uncorrected. Microanalytical data were obtained using a Fisons EA CHNS-O instrument ( $T = 1000$  °C). ESI mass spectra were obtained on a MS spectrometer HP 5989A using the direct insertion probe (DIP).  $^1H$  and  $^{13}C$  NMR spectra were recorded on a Varian VXR300 or a Varian VXR400 spectrometer, and peak positions are reported relative to TMS. The IR spectrum of the complex  $[Cd(NO_3)_2(L^5)]$ , required by one Referee, was recorded on a NICOLET 5700 FT-IR spectrophotometer. DMF was dried over  $MgSO_4$  and freshly distilled under reduced pressure. 2,9-Bis(chloromethyl)-1,10-phenanthroline (**1**),<sup>52</sup> *N*-*t*-butoxycarbonyl-bis(3-thioethyl)amine (**2**),<sup>53</sup> *N,N'*-bis(*p*-tolylsulphonyl)bis(2-aminoethyl)sulfide-*N,N'*-disodium salt (**3**),<sup>54</sup>  $L^1$ – $L^3$ ,<sup>39,42</sup>  $L^5$ ,<sup>44</sup> and  $L^6$  were prepared according to the reported procedures.<sup>55</sup> Other solvents and starting materials were purchased from commercial sources where available. **Caution!** Most of the reported metal complexes were isolated in the solid state as perchlorate salts. We have worked extensively with these complexes on a small scale without any incident. Despite these observations,

- (44) Arca, M.; Azimi, G.; Demartin, F.; Devillanova, F. A.; Escriche, L.; Garau, A.; Isaia, F.; Kivekas, R.; Lippolis, V.; Muns, V.; Perrera, A.; Shamsipur, M.; Sportelli, L.; Yari, A. *Inorg. Chim. Acta* **2005**, *238*, 2403.
- (45) De Filippo, G.; Demartin, F.; Garau, A.; Lippolis, V.; Yari, A.; Shokrollahi, A.; Shamsipur, M. *Inorg. Chim. Acta* **2005**, *358*, 801.
- (46) Shamsipur, M.; Javanbakht, M.; Mousavi, M. F.; Ganjali, M. R.; Lippolis, V.; Garau, A.; Tei, L. *Talanta* **2001**, *55*, 1047.
- (47) Shamsipur, M.; Javanbakht, M.; Ghasemi, Z.; Ganjali, M. R.; Lippolis, V.; Garau, A. *Sep. Purif. Technol.* **2002**, *28*, 141.
- (48) Shamsipur, M.; Javanbakht, M.; Lippolis, V.; Garau, A.; De Filippo, G.; Ganjali, M. R.; Yari, A. *Anal. Chim. Acta* **2002**, *462*, 225.
- (49) Shamsipur, M.; Javanbakht, M.; Ganjali, M. R.; Mousavi, M. F.; Lippolis, V.; Garau, A. *Electroanalysis* **2002**, *14*, 1691.
- (50) Shamsipur, M.; Kazemi, S. Y.; Azimi, G.; Madaeni, S. S.; Lippolis, V.; Garau, A.; Isaia, F. *J. Membr. Sci.* **2003**, *215*, 87.
- (51) Shamsipur, M.; Hashemi, O. R.; Lippolis, V. *J. Membr. Sci.* **2006**, *282*, 322.

- (52) Chandler, C. J.; Deady, L. W.; Reiss, J. A. *J. Heterocycl. Chem.* **1981**, *18*, 599.
- (53) Chartres, J. D.; Groth, A. M.; Lindoy, L. F.; Lowe, M. P.; Meehan, G. V. *J. Chem. Soc., Perkin Trans. 1* **2000**, 3444.
- (54) Hart, S. M.; Boeyens, J. C. A.; Michael, J. P.; Hancock, R. D. *J. Chem. Soc., Dalton Trans.* **1983**, 1601.
- (55) Shamsipur, M.; Hosseini, M.; Alizadeh, K.; Mousavi, M. F.; Garau, A.; Lippolis, V.; Yari, A. *Anal. Chem.* **2005**, *77*, 276.



the unpredictable behavior of perchlorate salts necessitates extreme care in handling.

**Synthesis of *N*-*t*-butoxycarbonyl 5-Aza-2,8-dithia[9]-(2,9)-1,10-phenanthroline (4).** A solution of 2,9-bis(chloromethyl)-1,10-phenanthroline (**1**) (0.58 g, 2.09 mmol) and *N*-*t*-butoxycarbonyl-bis(3-thioethyl)amine (**2**) (0.49 g, 2.06 mmol) in 50 mL of dry dimethylformamide (DMF) was added under N<sub>2</sub> over a period of 15 h to a stirred suspension of Cs<sub>2</sub>CO<sub>3</sub> (1.30 g, 3.99 mmol) in 180 mL of dry DMF at 55 °C. The resultant mixture was stirred at this temperature for a further 24 h and then for another 24 h at room temperature. The DMF was removed under reduced pressure, the residue taken up in CH<sub>2</sub>Cl<sub>2</sub> (100 mL), and the organic extract washed with water, dried, and concentrated under vacuum. The resulting brown residue was purified by flash-chromatography on silica gel using a mixture of CH<sub>2</sub>Cl<sub>2</sub>-CH<sub>3</sub>OH (9.5:0.5 v/v ratio) as eluent to give 0.45 g (49% yield) of **4** as a pale white product. Mp 148–150 °C. Elem. Anal. found. (calcd for C<sub>23</sub>H<sub>27</sub>N<sub>3</sub>O<sub>2</sub>S<sub>2</sub>): C, 62.3 (62.6); H, 6.5 (6.2); N, 9.4 (9.5); S, 14.5 (14.5)%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>), δ 1.42 (s, 9H), 2.69–2.74 (m, 4H), 3.41–3.51 (m, 4H), 4.19 (s, 4H), 7.75 (d, 2H, *J* = 8.4), 7.85 (s, 2H), 8.43 (d, 2H, *J* = 8.4 Hz). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>), δ 27.31, 28.41, 36.51, 47.93, 80.18, 122.91, 127.03, 128.68, 137.79, 145.43, 155.24, 157.23.

**Synthesis of 5-Aza-2,8-dithia[9]-(2,9)-1,10-phenanthroline (L<sup>4</sup>).** Trifluoroacetic acid (20 mL) was added to a solution of *N*-*t*-butoxycarbonyl 5-aza-2,8-dithia[9]-(2,9)-1,10-phenanthroline (**4**) (0.67 g, 1.52 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 mL), and the resulting solution was stirred at room temperature under N<sub>2</sub> for 2 h. The solvent was removed under reduced pressure and the residue taken up in water. The pH value was adjusted to 14 by adding 6 M NaOH and the product extracted into CH<sub>2</sub>Cl<sub>2</sub>. The organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure to give a white solid (0.35, 67% yield). Mp. 138 °C. Elem. Anal. found. (calcd for C<sub>18</sub>H<sub>19</sub>N<sub>3</sub>S<sub>2</sub>): C, 63.2 (63.3); H, 5.8 (5.6); N, 12.0 (12.3); S, 18.9 (18.8)%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 1.97 (s, 1H, CH<sub>2</sub>NHCH<sub>2</sub>), 2.68–2.73 (m, 4H, SCH<sub>2</sub>CH<sub>2</sub>N), 3.26–3.34 (m, 4H, SCH<sub>2</sub>CH<sub>2</sub>N), 4.17 (s, 4H, ArCH<sub>2</sub>S), 7.57 (d, 2H, *J* = 8.4), 7.76 (s, 2H), 8.22 (d, 2H, *J* = 8.4 Hz). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 27.60 (SCH<sub>2</sub>CH<sub>2</sub>N), 36.16 (ArCH<sub>2</sub>S), 47.10 (SCH<sub>2</sub>CH<sub>2</sub>N), 123.12, 126.03, 127.73, 137.70, 144.43, 157.59 (aromatic carbons). MS (ESI): *m/z* 341 ([C<sub>18</sub>H<sub>19</sub>N<sub>3</sub>S<sub>2</sub>]<sup>+</sup>).

**Synthesis of 2,8-Bis(p-tolylsulphonyl)-2,8-diaza-5-thia[9]-(2,9)-1,10-phenanthroline (5).** A solution of 2,9-bis(chloromethyl)-1,10-phenanthroline (**1**) (1.45 g, 5.2 mmol) in 50 mL of dry DMF was added under N<sub>2</sub> over a period of 5 h to a stirred suspension of *N,N'*-bis(p-tolylsulphonyl)bis(2-aminoethyl)sulfide-*N,N'*-disodium salt (**3**) (2.45 g, 5.2 mmol) in 100 mL of dry DMF heated to 105 °C. The resultant solution was stirred at this temperature for a further 24 h, cooled, and volume reduced to 50 mL. The mixture was poured into ice water, and the resulting precipitate collected by filtration and dissolved in CHCl<sub>3</sub> (100 mL). The organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and reduced under vacuum to give a yellow solid which was recrystallized from CHCl<sub>3</sub>-MeOH to give **5** as light yellow solid (2.47 g, 75% yield). Mp. 180 °C with decomposition. Elem. Anal. found. (calcd for C<sub>32</sub>H<sub>32</sub>N<sub>4</sub>O<sub>4</sub>S<sub>3</sub>): C, 60.4 (60.7); H, 4.9 (5.1); N, 9.0 (8.9); S, 14.8 (15.2)%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 2.42 (s, 6H), 2.85–2.93 (m, 4H), 3.44–3.52 (m, 4H), 4.77 (s, 4H), 7.30 (d, 4H, *J* = 8.0), 7.69–7.76 (m, 6H), 7.82 (s, 2H), 8.26 (d, 2H, *J* = 8.4 Hz). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 21.47, 30.78, 49.79, 53.86, 123.79, 126.49, 126.94, 128.0, 129.82, 137.01, 137.40, 143.47, 144.87, 156.15.

**Synthesis of 2,8-Diaza-5-thia[9]-(2,9)-1,10-phenanthroline (L<sup>7</sup>).** 2,8-Bis(p-tolylsulphonyl)-2,8-diaza-5-thia[9]-(2,9)-1,10-phenanthroline (**5**) (2.3 g, 3.6 mmol) was added to a solution of HBr in acetic acid (33%, 87 mL) and phenol (5.8 g, 61 mmol), and the solution was stirred at 75 °C for 48 h. A further portion of HBr in acetic acid (33%, 44 mL) was added, and the mixture stirred at 75 °C for a further 24 h. The reaction mixture was cooled, toluene was added, and the solvent was removed under reduced pressure. The residue was taken up in CH<sub>2</sub>Cl<sub>2</sub> (60 mL) and water (60 mL). The aqueous layer was separated, washed three times with CH<sub>2</sub>Cl<sub>2</sub>, and reduced under vacuum to a volume of about 5 mL. The solid obtained was recrystallized from EtOH-diethyl ether (3:1, v:v) and a white solid of formula L<sup>7</sup>·3HBr·H<sub>2</sub>O was obtained (1.0 g, 48% yield). This solid was taken up in water, the pH of the solution adjusted to 11 by adding 6 M KOH, and the product extracted into CHCl<sub>3</sub>. The organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure to give a white solid (0.35 g, 64% yield). Mp. 125 °C. Elem. Anal. found. (calcd for C<sub>18</sub>H<sub>20</sub>N<sub>4</sub>S): C, 66.3 (66.6); H, 6.2 (6.2); N, 16.9 (17.3); S, 9.6 (9.9)%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 3.05 (t, 4H, *J* = 6.4 Hz, NCH<sub>2</sub>CH<sub>2</sub>S), 3.49 (t, 4H, *J* = 6.4 Hz, NCH<sub>2</sub>CH<sub>2</sub>S), 4.64 (s, 4H, ArCH<sub>2</sub>N), 7.47 (s, 2H), 7.50 (d, 2H, *J* = 8.4), 8.10 (d, 2H, *J* = 8.4 Hz). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 29.92 (NCH<sub>2</sub>CH<sub>2</sub>S), 47.42 (NCH<sub>2</sub>CH<sub>2</sub>S), 50.98 (Ar-CH<sub>2</sub>N), 122.40, 126.40, 128.08, 138.20, 143.15, 151.24 (aromatic carbons). MS (ESI): *m/z* 324 ([C<sub>18</sub>H<sub>20</sub>N<sub>4</sub>S]<sup>+</sup>).

**Synthesis of Metal Complexes.** 1:1 metal complexes of L<sup>4</sup> and L<sup>7</sup> with Cu<sup>II</sup>, Zn<sup>II</sup>, Cd<sup>II</sup>, Pb<sup>II</sup>, Hg<sup>II</sup>, and Ag<sup>I</sup> have been synthesized by following a standard procedure which involves the mixing of the appropriate metal salt and the ligand (L<sup>4</sup> or L<sup>7</sup>) in 1:1 molar ratio in MeCN or MeOH and the isolation of the product as crystals or powder from the reaction mixture stirred for a few hours at room temperature, or under reflux, by diffusion of vapors of Et<sub>2</sub>O or evaporation of the solvent. Synthetic details including analytical data for the isolated complexes have been deposited as Supporting Information. As representative examples, the full synthetic procedures for the preparation of [Pb(L<sup>4</sup>)](ClO<sub>4</sub>)<sub>2</sub>·MeCN, [Cd(NO<sub>3</sub>)<sub>2</sub>(L<sup>5</sup>)], [Cu(L<sup>7</sup>)](ClO<sub>4</sub>)<sub>2</sub>·3/2MeNO<sub>2</sub>, [Pb(L<sup>7</sup>)](ClO<sub>4</sub>)<sub>2</sub>·1/2MeCN, which were also characterized by X-ray diffraction analysis, are reported below.

**Synthesis of [Pb(L<sup>4</sup>)](ClO<sub>4</sub>)<sub>2</sub>·MeCN.** A solution of Pb(ClO<sub>4</sub>)<sub>2</sub>·3H<sub>2</sub>O (0.027 g, 0.059 mmol) in MeCN was added to a solution of L<sup>4</sup> (0.020 g, 0.059 mmol) in MeCN (10 mL). The solution was stirred at room temperature under N<sub>2</sub> for 3 h. Colorless crystals were obtained by diffusion of Et<sub>2</sub>O vapor into the reaction mixture (0.035 g, yield 74%). Elem. Anal. found (calc for C<sub>20</sub>H<sub>22</sub>Cl<sub>2</sub>N<sub>4</sub>O<sub>8</sub>PbS<sub>2</sub>): C, 30.8 (30.5); H, 2.5 (2.8); N, 6.8 (7.1); S, 7.9 (8.1)%. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN): δ 2.52–2.62 (m, 2H), 2.89–3.11 (m, 4H), 3.31–3.38 (m, 2H), 4.65 (d, 2H, *J* = 17.6 Hz), 4.81 (d, 2H, *J* = 18.8 Hz), 8.10 (d, 2H, *J* = 8.4 Hz), 8.22 (s, 2H), 8.84 (d, 2H, *J* = 8.4 Hz). Electronic spectrum (MeCN): λ/nm (ε/M<sup>-1</sup> cm<sup>-1</sup>): 206 (44360), 232 (36100), 273 (20760), 301sh (9930).

**Synthesis of [Cd(NO<sub>3</sub>)<sub>2</sub>(L<sup>5</sup>)].** A solution of Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (0.016 g, 0.052 mmol) in MeCN was added to a solution of L<sup>5</sup> (0.020 g, 0.056 mmol) in MeCN (10 mL). The solution was stirred at room temperature under N<sub>2</sub> for 3 h. The white solid obtained was dissolved in MeNO<sub>2</sub> and light yellow crystals were obtained by diffusion of Et<sub>2</sub>O vapor into the solution (0.015 g, yield 45%). Elem. Anal. found (calcd for C<sub>19</sub>H<sub>21</sub>CdN<sub>5</sub>O<sub>6</sub>S<sub>2</sub>): C, 38.7 (38.6); H, 3.8 (3.6); N, 11.6 (11.8); S, 10.5 (10.8)%. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN): δ 1.49 (s, 3H, -CH<sub>3</sub>), 2.44–2.55 (m, 4H), 2.72–2.79 (m, 2H), 2.87–2.98 (m, 2H), 4.49 (d, 2H, *J* = 18.4 Hz), 4.76 (d, 2H,

$J = 18.0$  Hz), 8.06 (d, 2H,  $J = 8.4$  Hz), 8.26 (s, 2H), 8.81 (d, 2H,  $J = 8.4$  Hz). Electronic spectrum (MeCN):  $\lambda/\text{nm}$  ( $\epsilon/\text{M}^{-1} \text{cm}^{-1}$ ): 206 (37860), 232 (35460), 277 (22550), 297 sh (10020). IR spectrum (KBr disk): 3059w, 3014w, 2954w, 2913w, 2878w, 1616m, 1593s, 1533m, 1497s, 1384s, 1304s, 1206m, 1170m, 1105m, 1079m, 1037m, 986m, 892s, 856m, 816w, 786m, 721m  $\text{cm}^{-1}$ .

**Synthesis of  $[\text{Cu}(\text{L}^7)](\text{ClO}_4)_2 \cdot 3/2 \text{MeNO}_2$ .** A solution of  $\text{Cu}(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$  (0.018 g, 0.060 mmol) in EtOH was added to a solution of  $\text{L}^7$  (0.020 g, 0.062 mmol) in EtOH (10 mL). The solution was stirred at room temperature under  $\text{N}_2$  for 1 h. The light blue solid obtained was dissolved in  $\text{MeNO}_2$ , and blue crystals were obtained by diffusion of  $\text{Et}_2\text{O}$  vapor into the solution (0.025 g, yield 59%). Elem. Anal. found (calcd for  $\text{C}_{19.5}\text{H}_{24.5}\text{Cl}_2\text{CuN}_{5.5}\text{O}_{11}\text{S}$ ): C, 34.8 (34.5); H, 3.4 (3.6); N, 11.3 (11.4); S, 5.0 (4.7)%. Electronic spectrum (MeCN):  $\lambda/\text{nm}$  ( $\epsilon/\text{M}^{-1} \text{cm}^{-1}$ ): 214 (25420), 227sh (22130), 271 (18650), 299sh (7870), 605 (72.9).

**Synthesis of  $[\text{Pb}(\text{L}^7)](\text{ClO}_4)_2 \cdot 1/2 \text{MeCN}$ .**  $\text{Pb}(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$  (0.028 g, 0.061 mmol) in MeOH was added to a solution of  $\text{L}^7$  (0.020 g, 0.062 mmol) in MeOH (10 mL). The solution was stirred at reflux under  $\text{N}_2$  for 2 h. The white solid obtained was dissolved in MeCN and colorless crystals were obtained by slow evaporation at room temperature (0.039 g, yield 83%). Elem. Anal. found (calcd for  $\text{C}_{19}\text{H}_{21.5}\text{Cl}_2\text{N}_{4.5}\text{O}_8\text{PbS}$ ): C, 30.5 (30.4); H, 2.7 (2.9); N, 8.1 (8.4); S, 4.1 (4.3)%.  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  3.03–3.11 (m, 2H), 3.60–3.66 (m, 2H), 3.76–3.81 (m, 2H), 4.21–4.27 (m, 2H), 4.72–4.88 (m, 4H), 8.09 (d, 2H,  $J = 8.4$  Hz), 8.23 (s, 2H), 8.83 (d, 2H,  $J = 8.4$  Hz). Electronic spectrum (MeCN):  $\lambda/\text{nm}$  ( $\epsilon/\text{M}^{-1} \text{cm}^{-1}$ ): 205 (37460), 232 (32140), 280 (21210), 300sh (9710).

**Potentiometric Measurements.** All pH measurements ( $\text{pH} = -\log [\text{H}^+]$ ) employed for the determination of ligand protonation and metal complex stability constants were generally carried out in degassed 0.1 M  $\text{NMe}_4\text{NO}_3$  aqueous solution at  $298.1 \pm 0.1$  K by means of conventional titration experiments under an inert atmosphere to avoid carbonation of solutions during titration.<sup>26</sup> In the case of  $\text{Hg}^{\text{II}}$  complexation, potentiometric measurements were also performed in degassed 0.1 M  $\text{NMe}_4\text{Cl}$  aqueous solutions at  $298.1 \pm 0.1$  K. The combined Ingold 405 S7/120 electrode was calibrated as a hydrogen concentration probe by titrating known amounts of HCl with  $\text{CO}_2$ -free  $\text{NMe}_4\text{OH}$  solutions and determining the equivalent point by Gran's method<sup>56</sup> which allows one to determine the standard potential  $E^\circ$  and the ionic product of water [ $\text{p}K_w = 13.83(1)$  and  $13.73(1)$  at  $298.1 \pm 0.1$  K in 0.1 M  $\text{NMe}_4\text{NO}_3$  and 0.1 M  $\text{NMe}_4\text{Cl}$ , respectively]. At least three measurements (with about 100 data points for each) were performed for each system over the pH range 2.0–11.0. In all experiments the ligand concentration  $[\text{L}]$  was about  $1 \times 10^{-3}$  M. In the complexation experiments the metal ion concentration was  $[\text{M}^{\text{II}}] = 0.8[\text{L}]$  ( $\text{L} = \text{L}^4, \text{L}^7$ ). The computer program HYPERQUAD<sup>57</sup> was used to calculate the equilibrium constants from e.m.f. data. For the determination of the stability constants of the  $\text{Hg}^{\text{II}}$  complexes, the stability of the  $\text{Hg}^{\text{II}}$  complexes with chloride were taken from ref 58.

**$^1\text{H}$  NMR Titrations.**  $^1\text{H}$  NMR titrations were carried out by addition of increasing amounts of perchlorate or nitrate salts of the different metals to a  $1 \times 10^{-3}$  M solution of the ligands in a  $\text{CD}_3\text{CN}/\text{D}_2\text{O}$  4:1 (v/v) mixture at  $\text{pD} = 7.0$  and  $25^\circ\text{C}$ . The  $\text{pD}$  of the solutions was adjusted to 7.0 by the additions of small volumes of 0.01 M DCl or NaOD. Peak positions are reported relative to TMS.

**Liquid–Liquid-Extraction.** The liquid–liquid extraction experiments were performed at  $21 \pm 1^\circ\text{C}$  in microcentrifuge tubes (2 mL) by means of mechanical overhead shaking. The phase ratio  $V_{(\text{org})}/V_{(\text{w})}$  (500  $\mu\text{L}$  each) was 1:1. In general a shaking time of 30 min was chosen, because the equilibrium was reached in this period. In the aqueous phase the initial metal ion concentration was  $1 \times 10^{-4}$  M. To keep the ionic strength constant  $\text{NaClO}_4$  was added in concentration of  $5 \times 10^{-3}$  M. The pH of the aqueous solution was adjusted using citric acid/NaOH and 4-morpholinoethanesulfonic acid (MES)/NaOH buffer solution. The equilibrium pH was measured by using an InLab micro pH electrode.  $\text{CHCl}_3$  was used as organic phase, and a ligand concentration of  $1 \times 10^{-3}$  M was used. In the competitive  $\text{Ag}^{\text{I}}$  extraction experiments with various metal ions a ligand concentration of  $1 \times 10^{-4}$  M was used. After the extraction, all samples were centrifuged, and the phases separated. The distribution of  $\text{Ag}^{\text{I}}$  and  $\text{Zn}^{\text{II}}$  was detected in both phases radiometrically by  $\gamma$ -radiation of  $^{110\text{m}}\text{Ag}$  and  $^{65}\text{Zn}$  in a NaI (TI) scintillation counter (Cobra II/Canberra-Packard). The concentrations of  $\text{Cu}^{\text{II}}$ ,  $\text{Zn}^{\text{II}}$ ,  $\text{Cd}^{\text{II}}$ ,  $\text{Pb}^{\text{II}}$ , and  $\text{Hg}^{\text{II}}$  in the single and multielement experiments were detected only by determination of the metal content in the water phase using the ICP-OES technique (ICP-OES-Optima 4300DV, Perkin-Elmer).

The easily accessible experimental parameter in liquid–liquid extraction systems are the distribution ratio ( $D_M$ ), the quotient of the metal concentrations in the organic and aqueous phase, or the percentage extraction ( $E\%$ ):  $D_M = C_{\text{M}(\text{org})}/C_{\text{M}(\text{w})}$ ;  $E[\%] = 100 \times D_M/(D_M + 1)$ , respectively.<sup>59</sup>

**Crystallography.** A summary of the crystal data and refinement details for the compounds discussed in this paper is given in Table 1. Only special features of the analyses are mentioned here. The single-crystal data for  $[\text{Cd}(\text{NO}_3)_2(\text{L}^5)]$ ,  $[\text{Pb}(\text{L}^7)](\text{ClO}_4)_2 \cdot 1/2 \text{MeCN}$ ,  $[\text{Pb}(\text{L}^4)](\text{ClO}_4)_2 \cdot \text{MeCN}$ , and  $[\text{Cu}(\text{L}^7)](\text{ClO}_4)_2 \cdot 3/2 \text{MeNO}_2$  were collected at room temperature on a Bruker SMART CCD diffractometer using graphite-monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) via  $\omega$  scans. Data sets were corrected for Lorentz-polarization effects and for absorption (Table 1). All structures were solved by direct methods using SHELXS 97<sup>61</sup> and completed by iterative cycles of full-matrix least-squares refinement and  $\Delta F$  synthesis using SHELXL 97.<sup>62</sup> All non-H atoms were refined anisotropically. All H atoms were placed in calculated positions and refined using a riding model. The acetonitrile molecule in  $[\text{Pb}(\text{L}^7)](\text{ClO}_4)_2 \cdot 1/2 \text{MeCN}$  was found to be disordered about a 2-fold axis. A structural model with this molecule ordered could be achieved by refining the structure in the space group  $P\bar{1}$ , corresponding to the primitive cell with  $a = 12.772(1)$ ,  $b = 12.794(1)$ ,  $c = 15.243(2) \text{ \AA}$ ,  $\alpha = 83.37(1)$ ,  $\beta = 83.99(1)$ ,  $\gamma = 87.32(1)^\circ$  and containing two independent  $[\text{Pb}(\text{L}^7)]^{2+}$  cations and four independent  $\text{ClO}_4^-$  anions in the asymmetric unit. However, because most of the structure conforms to the space group  $C2/c$ , the only exception being the acetonitrile molecule, the description in this setting was preferred, in view of a more favorable observation/parameters ratio. The structure of  $[\text{Pb}(\text{L}^4)](\text{ClO}_4)_2 \cdot \text{MeCN}$  was affected by non-merohedral twinning which was treated by producing a SHELXL

(56) Gran, G. *Analyst (London)* **1952**, *77*, 661.

(57) Gans, P.; Sabatini, A.; Vacca, A. *Talanta* **1996**, *43*, 807.

(58) Smith, R. M.; Martell, A. M. *NIST Stability Constants Database*, version 4.0; National Institute of Standards and Technology: Washington, DC, 1997.

(59) Stephan, H.; Juran, S.; Antonioli, B.; Gloe, K. In *Analytical Methods in Supramolecular Chemistry* Schalley, Ch., Ed.; Wiley-VCH: Weinheim, 2006; pp 79–103; ISBN 3-527-31505-5.

(60) *SADABS, Area-Detector Absorption Correction Program*; Bruker AXS, Inc.: Madison, WI, 2003.

(61) Sheldrick, G. M. *Acta Crystallogr. Sect. A* **1990**, *46*, 467; SHELXS 86–97.

(62) Sheldrick, G. M. SHELXL 97; University of Göttingen: Göttingen, Germany, 1998.

**Table 1.** Crystallographic Data for [Cd(NO<sub>3</sub>)<sub>2</sub>(L<sup>5</sup>)], [Pb(L<sup>4</sup>)](ClO<sub>4</sub>)<sub>2</sub>·MeCN, [Pb(L<sup>7</sup>)](ClO<sub>4</sub>)<sub>2</sub>·<sup>1</sup>/<sub>2</sub>MeCN, and [Cu(L<sup>7</sup>)](ClO<sub>4</sub>)<sub>2</sub>·<sup>3</sup>/<sub>2</sub>MeNO<sub>2</sub>

	[Cd(NO <sub>3</sub> ) <sub>2</sub> (L <sup>5</sup> )]	[Pb(L <sup>4</sup> )](ClO <sub>4</sub> ) <sub>2</sub> ·MeCN	[Pb(L <sup>7</sup> )](ClO <sub>4</sub> ) <sub>2</sub> · <sup>1</sup> / <sub>2</sub> MeCN	[Cu(L <sup>7</sup> )](ClO <sub>4</sub> ) <sub>2</sub> · <sup>3</sup> / <sub>2</sub> MeNO <sub>2</sub>
formula	C <sub>19</sub> H <sub>21</sub> CdN <sub>5</sub> O <sub>6</sub> S <sub>2</sub>	C <sub>20</sub> H <sub>22</sub> Cl <sub>2</sub> N <sub>4</sub> O <sub>8</sub> PbS <sub>2</sub>	C <sub>38</sub> H <sub>43</sub> Cl <sub>4</sub> N <sub>9</sub> O <sub>16</sub> Pb <sub>2</sub> S <sub>2</sub>	C <sub>39</sub> H <sub>49</sub> Cl <sub>4</sub> Cu <sub>2</sub> N <sub>11</sub> O <sub>22</sub> S <sub>2</sub>
crystal system	trigonal	triclinic	monoclinic	monoclinic
space group	R $\bar{3}$ (No. 148)	P $\bar{1}$ (No. 1)	C2/c (No. 15)	P2 <sub>1</sub> /n (No. 14)
M.W.	591.93	788.63	1502.11	1356.89
a /Å	41.363(8)	11.353(2)	18.496(2)	15.423(3)
b /Å	41.363(8)	15.405(2)	17.650(2)	10.812(2)
c /Å	8.056(2)	15.708(3)	15.243(2)	32.708(7)
α /deg	90.00	67.219(2)	90.00	90.00
β /deg	90.00	89.697(2)	98.75(1)	99.080(10)
γ /deg	120.00	87.778(2)	90.00	90.00
V /Å <sup>3</sup>	11936(4)	2530.9(7)	4918.2(1)	5385.8(18)
Z	18	4	4	4
T /K	294(2)	150(2)	294(2)	294(2)
D <sub>c</sub> /g cm <sup>-3</sup>	1.482	2.070	2.029	1.668
μ/mm <sup>-1</sup>	1.021	7.097	7.217	1.154
unique reflections, R <sub>int</sub>	5227, 0.055	10763, 0.095	4872, 0.092	15696, 0.039
observed reflections [I > 2σ(I)]	4164	7639	2924	8867
absorption correction	SADABS <sup>60</sup>	SADABS <sup>60</sup>	SADABS <sup>60</sup>	SADABS <sup>60</sup>
T <sub>min</sub> , T <sub>max</sub>	0.807, 1.000	0.028, 1.000	0.511, 1.000	0.725, 1.000
R <sub>1</sub>	0.0869	0.0756	0.0588	0.0693
wR <sub>2</sub> [all data]	0.249	0.242	0.097	0.224

HKLF 5 file: the twin law was (1 -0.064 0.017/0 -1 0/0 0 -1) and the twin fraction refined to 0.130(2). Perchlorate anions were seriously affected by disorder which was modeled using alternative atom sites and refined with distance, angle, and similarity restraints; oxygen atoms in the disordered perchlorate anions were refined isotropically. Similarity restraints were also applied between the two independent L<sup>4</sup> molecules. One of the three MeNO<sub>2</sub> molecules in the asymmetric unit of [Cu(L<sup>7</sup>)](ClO<sub>4</sub>)<sub>2</sub>·<sup>3</sup>/<sub>2</sub>MeNO<sub>2</sub> was found to exhibit disorder. The disorder was modeled without restraints (a model with restraints offering no advantage) by considering the carbon atom fully occupied and by splitting the nitrogen and oxygen atoms into two components and setting the occupancy of each disordered site to 0.5. No H atoms were placed on the carbon atom of the disordered MeNO<sub>2</sub> molecule.

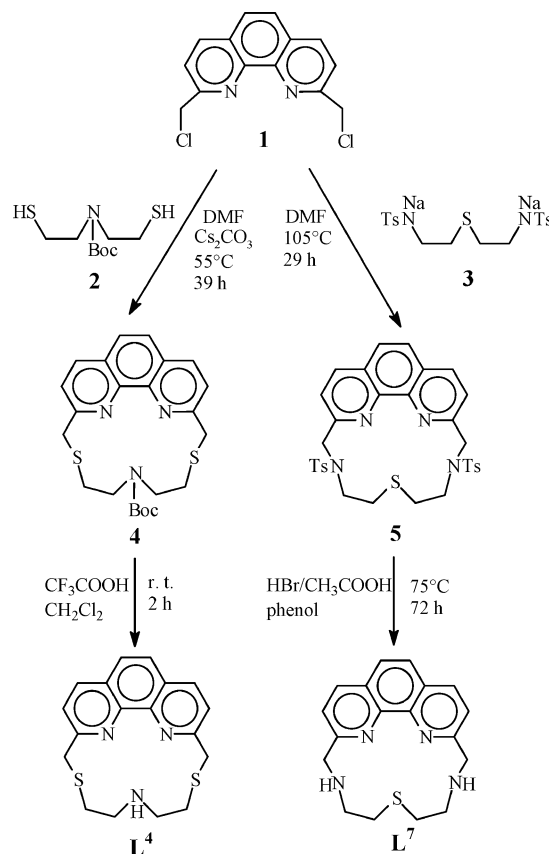
## Results and Discussion

**Synthesis and Coordination Properties in Solution.** The strategy adopted in the synthesis of L<sup>4</sup> and L<sup>7</sup> very much resembles that used for the preparation of L<sup>1</sup>-L<sup>3</sup> and L<sup>5</sup> and L<sup>6</sup> (Figure 2)<sup>39,42,44,55</sup> A cyclization reaction performed under high dilution conditions between 2,9-bis(chloromethyl)-1,10-phenanthroline (1)<sup>52</sup> and *N*-*t*-butoxycarbonyl-bis(3-thioethyl)amine (2, for L<sup>4</sup>),<sup>53</sup> or *N,N'*-bis(*p*-tolylsulphonyl)bis(2-aminoethyl)sulfide-*N,N'*-disodium salt (3, for L<sup>7</sup>),<sup>54</sup> in DMF, followed by deprotection of the secondary nitrogen atom(s), affords the required macrocyclic ligands, L<sup>4</sup> and L<sup>7</sup> with overall yields of 33 and 48%, respectively.

The key feature of these two ligands, in contrast to the others shown in Figure 1, is the presence of secondary nitrogen atoms in the macrocyclic framework: this renders the two compounds sufficiently soluble in water to allow a potentiometric study of their protonation and complexation to metal ions in this solvent. For L<sup>1</sup>-L<sup>3</sup> and L<sup>5</sup> solution studies of their complexation properties toward Pb<sup>II</sup>, Cd<sup>II</sup>, Hg<sup>II</sup>, Cu<sup>II</sup>, and Ag<sup>I</sup> using spectrophotometric, fluorimetric, and conductometric measurements were only possible in MeCN because of their insolubility in water (Supporting Information, Table S1).<sup>42,45</sup> The formation of 1:1 metal complexes was observed for all combinations of ligand and metal ion considered, with stability constants of the same

order of magnitude.<sup>42,45</sup> The formation of 1:2 metal-to-ligand complexes was only observed in solution with Pb<sup>II</sup> (L<sup>3</sup>), Hg<sup>II</sup> (L<sup>1</sup>, L<sup>2</sup>), and Cd<sup>II</sup> (L<sup>2</sup>, L<sup>3</sup>), and the X-ray crystal structure of [Pb(L<sup>3</sup>)<sub>2</sub>][ClO<sub>4</sub>]<sub>2</sub>·2MeCN was determined.<sup>42</sup>

Ligand protonation and complex formation of L<sup>4</sup> and L<sup>7</sup> with Cu<sup>II</sup>, Zn<sup>II</sup>, Cd<sup>II</sup>, Pb<sup>II</sup>, and Hg<sup>II</sup> were investigated by means of potentiometric measurements in aqueous solutions (NMe<sub>4</sub>NO<sub>3</sub> 0.1 M, 298.1 K) in the pH range 2.5–10.5 (Cu<sup>II</sup> and Cd<sup>II</sup> with L<sup>4</sup>, and Zn<sup>II</sup>, Cd<sup>II</sup> and Pb<sup>II</sup> with L<sup>7</sup>) or 2.5–7.0 (Cu<sup>II</sup> with L<sup>7</sup>). In this latter case, precipitation of hydroxo-



**Figure 2.** Reagents and experimental conditions for the synthesis of L<sup>4</sup> and L<sup>7</sup>.



**Table 2.** Protonation Constants of **L**<sup>4</sup> and **L**<sup>7</sup> and Stability Constants of Their Metal Complexes in Water (NMe<sub>4</sub>NO<sub>3</sub> 0.1 M or NMe<sub>4</sub>Cl 0.1 M, 298.1 K)

reaction	log K					
	<b>L</b> <sup>4</sup>		<b>L</b> <sup>7</sup>			
$L + H^+ \rightleftharpoons (HL)^+$	8.3(1)					8.65(1)
$(HL)^+ + H^+ \rightleftharpoons (H_2L)^{2+}$	2.3(1)					7.34(1)
$(HL)^{2+} + H^+ \rightleftharpoons (H_3L)^{3+}$						1.94(2)

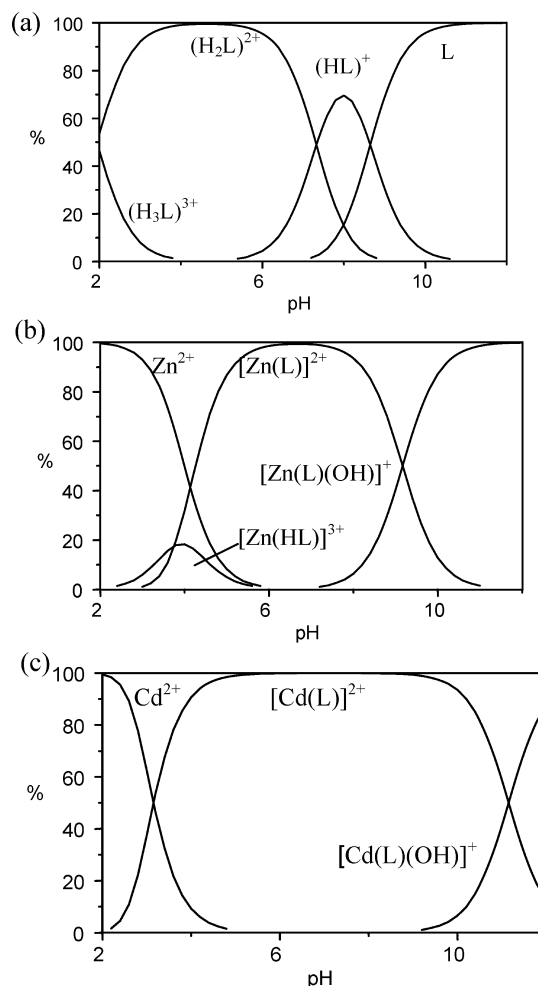
  

reaction	log K					
	Cu <sup>IIa</sup>	Zn <sup>IIa</sup>	Cd <sup>IIa</sup>	Pb <sup>IIa</sup>	Hg <sup>IIa</sup>	Hg <sup>IIb</sup>
$M^{2+} + L^4 \rightleftharpoons [M(L^4)]^{2+}$	10.9(1)	c	11.2(1)	c	> 15	21.3(1)
$[M(L^4)]^{2+} + OH^- \rightleftharpoons [M(L^4)(OH)]^+$	4.7(1)		3.54(1)			d
$M^{2+} + L^7 \rightleftharpoons [M(L^7)]^{2+}$	15.21(2)	11.09(1)	13.00(1)	13.46(1)	> 17	23.7(1)
$[M(L^7)]^{2+} + H^+ \rightleftharpoons [M(HL^7)]^{3+}$		3.76(2)				
$[M(L^7)]^{2+} + OH^- \rightleftharpoons [M(L^7)(OH)]^+$	d	4.66(3)	2.67(2)	3.07(1)		d

<sup>a</sup> NMe<sub>4</sub>NO<sub>3</sub> 0.1 M. <sup>b</sup> NMe<sub>4</sub>Cl 0.1 M. <sup>c</sup> The low solubility of the Zn<sup>II</sup> and Pb<sup>II</sup> complexes with **L**<sup>4</sup> does not allow the potentiometric study of these systems. The same happened for the complexes of Ag<sup>I</sup> with both **L**<sup>4</sup> and **L**<sup>7</sup>. <sup>d</sup> Precipitation at slightly alkaline pH values of hydroxo-complexes does not allow the study of the system in the alkaline pH region.

complexes at slightly alkaline pH values precluded the study of the system in the alkaline pH region. The Hg<sup>II</sup> complexes with both ligands were completely formed even at pH 2.5 in a 0.1 M NMe<sub>4</sub>NO<sub>3</sub> aqueous solution and therefore their formation constants could only be estimated as higher than 15 and 17 log units for [Hg(**L**<sup>4</sup>)]<sup>2+</sup> and [Hg(**L**<sup>7</sup>)]<sup>2+</sup>, respectively. However, it was possible to determine the formation constants of the 1:1 Hg<sup>II</sup> complexes with **L**<sup>4</sup> and **L**<sup>7</sup> in 0.1 M NMe<sub>4</sub>Cl solutions because of the presence in these solutions of competitive complexation equilibria of Hg<sup>II</sup> with the chloride ion. The study of these systems at alkaline pH values was not possible because of precipitation of hydroxo-complexes. Finally, Zn<sup>II</sup> and Pb<sup>II</sup> complexation with **L**<sup>4</sup> and Ag<sup>I</sup> complexation with **L**<sup>4</sup> and **L**<sup>7</sup> could not be studied by potentiometry because of complex precipitation at acidic pH values. Protonation constants and stability constants of the complexes formed are reported in Table 2, while Figure 3 shows the distribution diagram for the protonated forms of **L**<sup>7</sup> and for the Zn<sup>II</sup> and Cd<sup>II</sup> complexes with **L**<sup>7</sup> (the distribution diagram for the protonated form of **L**<sup>4</sup>, for the Cu<sup>II</sup> and Cd<sup>II</sup> complexes with **L**<sup>4</sup>, for the Cu<sup>II</sup> and Pb<sup>II</sup> complexes with **L**<sup>7</sup>, and for the Hg<sup>II</sup> complexes with **L**<sup>4</sup> and **L**<sup>7</sup> are supplied as Supporting Information, Figure S1, Figure S2 and Figure S3, respectively).

**L**<sup>7</sup> can bind up to three protons in aqueous solution. The first two protonation constants are far higher than that reported for the protonation of 1,10-phenanthroline alone (log K = 4.96),<sup>63</sup> suggesting that the first two protonation steps occur on the secondary amine groups in the aliphatic chain. The first protonation constant, however, is lower than those generally found for protonation of secondary amine groups in macrocyclic polyamines (9–10 log units),<sup>64</sup> probably because of the electron-withdrawing effect exerted by the heteroaromatic unit, which reduces the proton binding ability of the adjacent aliphatic amine groups. The third protonation step involves the phenanthroline nitrogen atoms and occurs only at strongly acidic pH (Figure 3a), as their basicity is reduced by the presence of two already protonated amine groups in the molecule. Similar considerations apply to **L**<sup>4</sup>,

**Figure 3.** Distribution diagrams for the systems H<sup>+</sup>/**L**<sup>7</sup> (a), Zn<sup>II</sup>/**L**<sup>7</sup> (b), and Cd<sup>II</sup>/**L**<sup>7</sup> (c) in water ([M<sup>II</sup>] = [L<sup>7</sup>] = 1 × 10<sup>-3</sup> M, 298.1 K; I = 0.1 M).

where the values of the two protonation constants account respectively for protonation of the single aliphatic amine group at alkaline pH values and of the phenanthroline unit in the acidic pH region.

On passing to metal complexation, **L**<sup>7</sup> forms stable complexes with all the metal ions under investigation. As shown in Figure 3b and 3c for Zn<sup>II</sup> and Cd<sup>II</sup> complexation, respectively, metal complexation occurs at acidic pH values

(63) Condikey, G.; Martell, A. E. *J. Inorg. Nucl. Chem.* **1969**, *31*, 2455.

(64) Bencini, A.; Bianchi, A.; Garcia-España, E.; Micheloni, M.; Ramirez, J. A. *Coord. Chem. Rev.* **1999**, *188*, 97.

and is followed by deprotonation of coordinated water molecules to give the monohydroxo-complex species  $[\text{ML}^7(\text{OH})]^+$  in the alkaline pH region. In the case of  $\text{Cu}^{\text{II}}$ , precipitation at alkaline pH prevents the study of the formation of hydroxo-complexes.  $\text{Zn}^{\text{II}}$  displays the highest tendency to form a monohydroxo-complex, as would be expected from the higher acidity of this ion with respect to  $\text{Cd}^{\text{II}}$  and  $\text{Pb}^{\text{II}}$ .

The binding ability of  $\text{L}^7$  toward the different metals can be seen in the values of the stability constants which increase in the order  $\text{Zn}^{\text{II}} < \text{Cd}^{\text{II}} \approx \text{Pb}^{\text{II}} < \text{Cu}^{\text{II}} < \text{Hg}^{\text{II}}$ . As is generally found for complexes with polyamine ligands,<sup>58</sup>  $\text{Hg}^{\text{II}}$  forms the most stable complex because of its high affinity for nitrogen and sulfur donor atoms. At the same time, the fact that the observed stability of the complex with  $\text{Cu}^{\text{II}}$  is higher than those with the  $d^{10}$   $\text{Zn}^{\text{II}}$ ,  $\text{Cd}^{\text{II}}$ , and  $\text{Pb}^{\text{II}}$  cations can be simply related to the stabilizing effect of CFSE for the  $d^9$   $\text{Cu}^{\text{II}}$  ion. In contrast, the lower stability of the  $\text{Zn}^{\text{II}}$  complex with respect to the  $\text{Cd}^{\text{II}}$  and  $\text{Pb}^{\text{II}}$  ones is less usual because polyamine ligands often show a similar binding ability toward these metals. This experimental result could simply be ascribed to the presence within the macrocyclic framework of the “soft” sulfur donor, which generally displays a higher binding affinity toward the softer  $\text{Cd}^{\text{II}}$  and  $\text{Pb}^{\text{II}}$  cations. However, a better size match between the macrocyclic cavity and the larger  $\text{Cd}^{\text{II}}$  and  $\text{Pb}^{\text{II}}$  ions could also contribute to the higher stability of their complexes with respect to  $\text{Zn}^{\text{II}}$ . This hypothesis is supported by the higher binding ability toward  $\text{Cd}^{\text{II}}$  and  $\text{Pb}^{\text{II}}$  displayed by the ligand 2,5,8-triaza[9]-(2,9)-1,10-phenanthroline, where a secondary amine group replaces the sulfur donor of  $\text{L}^7$  ( $\log K = 16.15$ ,<sup>65</sup> 17.30,<sup>66</sup> and 18.70<sup>67</sup> for the  $\text{Zn}^{\text{II}}$ ,  $\text{Cd}^{\text{II}}$ , and  $\text{Pb}^{\text{II}}$  complexes with this ligand).

The extent of the comparison between the binding ability of  $\text{L}^7$  and  $\text{L}^4$  is limited by the fact that only the stability constants for the  $\text{Cu}^{\text{II}}$ ,  $\text{Cd}^{\text{II}}$ , and  $\text{Hg}^{\text{II}}$  complexes with  $\text{L}^4$  can be determined. The data in Table 2, however, show a dramatic decrease in the stability of the  $\text{Cu}^{\text{II}}$ ,  $\text{Cd}^{\text{II}}$ , and  $\text{Hg}^{\text{II}}$  complexes on passing from  $\text{L}^7$  to  $\text{L}^4$ . This behavior can reasonably be ascribed to the general lower affinity of sulfur donors for these metals with respect to amine donors. It is noteworthy that the decrease in stability is considerably greater in the case of  $\text{Cu}^{\text{II}}$  complexation ( $\log K = 15.21$  and 10.9 for the formation of the  $\text{Cu}^{\text{II}}$  complexes with  $\text{L}^7$  and  $\text{L}^4$ , respectively) than for  $\text{Cd}^{\text{II}}$  and  $\text{Hg}^{\text{II}}$  complexation (for instance,  $\log K = 13.00$  and 11.2 for the formation of the  $\text{Cd}^{\text{II}}$  complexes with  $\text{L}^7$  and  $\text{L}^4$ , respectively); this observation can be rationalized, once again, by considering the softer characteristics of  $\text{Cd}^{\text{II}}$  and  $\text{Hg}^{\text{II}}$ ; in fact, it is expected that the replacement of an amine group of  $\text{L}^7$  with a softer sulfur donor in  $\text{L}^4$  would lead to a less pronounced decrease in stability in the case of the softer  $\text{Cd}^{\text{II}}$  and  $\text{Hg}^{\text{II}}$  metal ions.

Metal complexations of  $\text{L}^4$  and  $\text{L}^7$  were also followed by means of  $^1\text{H}$  NMR titrations carried out by adding increasing amounts of a metal salt to a solution of the ligand in a  $\text{CD}_3\text{CN}/\text{D}_2\text{O}$  4:1 (v/v) mixture at  $\text{pD} = 7.0$  and  $25^\circ\text{C}$ , with the aim to ascertain the stoichiometry of the complexes formed in solution. Unfortunately, it was not possible to perform  $^1\text{H}$  NMR titrations in  $\text{D}_2\text{O}$  because of the very low solubility of all complexes in this medium. Conversely, the  $\text{CD}_3\text{CN}/\text{D}_2\text{O}$  4:1 (v/v) mixture ensured simultaneously solubility of the ligands and no precipitation of the complexes during titrations. However, the highest concentration achieved for the ligands was only  $1 \times 10^{-3}$  M.

The  $^1\text{H}$  NMR spectra of  $\text{L}^4$  and  $\text{L}^7$  alone display a set of three signals for the protons belonging to the phenanthroline moiety (two doublets and a singlet) and a second set of three signals for the aliphatic fragment (a singlet that can be assigned to the methylene groups adjacent to the phenanthroline moiety and two triplets for the ethylenic chains) each integrating for four protons, in agreement with a  $C_{2v}$  time-averaged symmetry in solution. Complexation strongly affects the  $^1\text{H}$  NMR spectral features of both  $\text{L}^4$  and  $\text{L}^7$ . In the case of  $\text{Zn}^{\text{II}}$  and  $\text{Hg}^{\text{II}}$  and for both ligands, addition of 0.25 equiv of these metal ions already causes the appearance of a new set of signals, which can be attributed to the formation of the corresponding complexes slowly interchanging with the free ligands on the NMR time scale. The new signals are generally shifted downfield by 0.05–0.2 ppm with respect to those of the free ligands observed under the same conditions (see Supporting Information, Table S2 for a list of the  $^1\text{H}$  chemical shifts of the complexes). While the signals of the phenanthroline protons in the complexes are sharp and clearly distinguishable from those in the ligands during titrations (see Figure 4a for the system  $\text{Hg}^{\text{II}}/\text{L}^7$ ), the signals of the aliphatic protons of the complexes are generally unstructured, broad, and partially superimposed either on the signals of the free ligands or on the signal from HOD at 3.88 ppm. These features might indicate the presence in solution of interchanging conformers, probably differing slightly in the conformation adopted by the aliphatic chains around the metal cations and characterized by lifetimes similar to the time scale of the  $^1\text{H}$  experiments. The signals in the aromatic region do not seem to be affected by this interconversion process.

Addition of increasing amounts of  $\text{Zn}^{\text{II}}$  or  $\text{Hg}^{\text{II}}$  leads to a progressive increase in the intensity of the phenanthroline signals corresponding to the metal complexes formed and to a simultaneous decrease in the intensity of the resonances of the ligands. At a 1:1 metal-to-ligand molar ratio, the set of resonances of the free ligands disappears completely, and the spectra show only the signals of the metal complexes. Further addition of metal ions does not change these spectral features. These data account for the formation of stable 1:1 complexes between the ligands and  $\text{Zn}^{\text{II}}$  and  $\text{Hg}^{\text{II}}$ .<sup>68</sup>

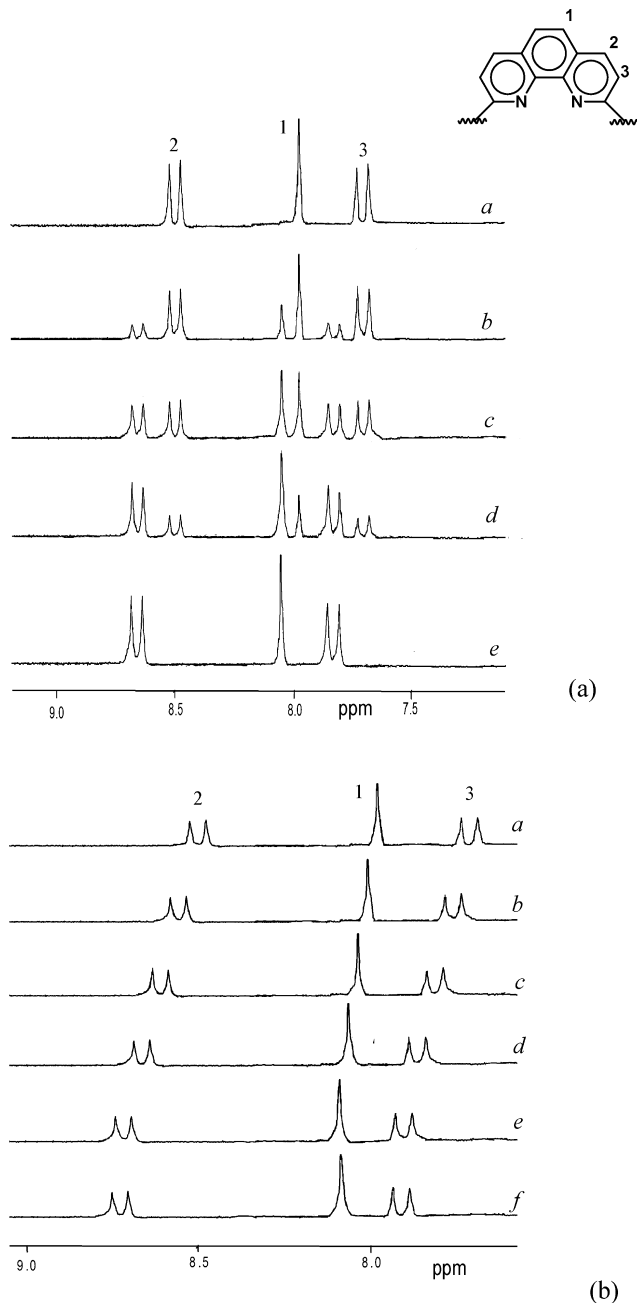
(65) Bazzicalupi, C.; Bencini, A.; Bianchi, A.; Giorgi, C.; Fusi, V.; Valtancoli, B.; Bernardo, M. A.; Pina, F. *Inorg. Chem.* **1999**, *38*, 3806.

(66) Bencini, A.; Bianchi, A.; Fornasari, P.; Giorgi, C.; Paoletti, P.; Valtancoli, B. *Polyhedron*. **2002**, *21*, 1329.

(67) Bazzicalupi, C.; Bencini, A.; Giorgi, C.; Fusi, V.; Paoletti, P.; Valtancoli, B. *Dalton Trans.* **1999**, 393.

(68) The high stability of the complexes and the low solubility of  $\text{L}^4$ ,  $\text{L}^7$  and their metal complexes prevents a reliable determination of the stability constants of the complexes by using  $^1\text{H}$  NMR titrations at a fixed pD value.





**Figure 4.** (a)  $^1\text{H}$  NMR spectra of  $\text{L}^7$  in the presence of increasing amounts of  $\text{Hg}^{\text{II}}$  in  $\text{CD}_3\text{CN}/\text{D}_2\text{O}$  4:1 (v/v) at  $\text{pD} = 7.0$  [ $\text{Hg}^{\text{II}}/\text{L}^7$  molar ratio: 0.0 (a), 0.25 (b), 0.50 (c), 0.75 (d), 1.0 (e)]. (b)  $^1\text{H}$  NMR spectra of  $\text{L}^7$  in the presence of increasing amounts of  $\text{Pb}^{\text{II}}$  at  $\text{pD} = 7.0$  [ $\text{Pb}^{\text{II}}/\text{L}^7$  molar ratio: 0.0 (a), 0.25 (b), 0.50 (c), 0.75 (d), 1.0 (e), 1.25 (f)];  $[\text{L}^7] = 1 \times 10^{-3}$  M, 298.1 K.

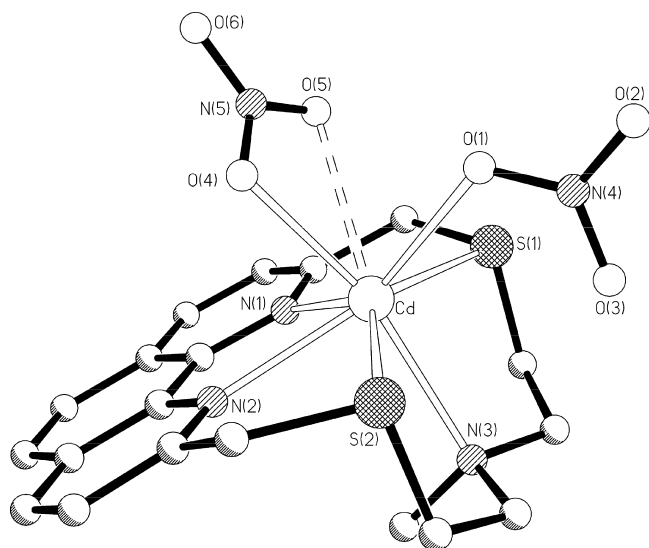
In the case of  $\text{Cd}^{\text{II}}$ ,  $\text{Pb}^{\text{II}}$ , and  $\text{Ag}^{\text{I}}$ , and for both ligands, addition of increasing amounts of these metal cations leads a progressive downfield shift of the  $^1\text{H}$  signals up to a 1:1 metal-to-ligand molar ratio (see Figure 4b for the system  $\text{Pb}^{\text{II}}/\text{L}^7$ ). Further addition of the metals does not change the spectra. This suggests the formation of mononuclear metal complexes which are undergoing fast exchange with the free ligands in solution.<sup>68</sup> The signals of the aliphatic protons shift and broaden upon metal complexation. Unfortunately, the low solubility of the complexes did not allow an NMR study at lower temperatures.

On the other hand, the  $^1\text{H}$  NMR spectra of the 1:1 metal-to-ligand complexes isolated in the solid state and recorded in  $\text{CD}_3\text{CN}$  solution at 25 °C (where the solubility for some of the complexes was lower than  $1 \times 10^{-3}$  M) in some cases showed more complex patterns of generally broad signals in the aliphatic region which might suggest a lowering, in this medium, of the time-averaged symmetry of the ligands upon metal complexation (see Experimental Section and Supporting Information).

In particular, the 1:1 complexes of  $\text{Hg}^{\text{II}}$  and  $\text{Cd}^{\text{II}}$  with  $\text{L}^4$ , and the 1:1 complexes of  $\text{Zn}^{\text{II}}$  and  $\text{Ag}^{\text{I}}$  with  $\text{L}^7$  present two distinct groups of signals for the aliphatic protons of the ethylenic fragments, each integrating for four protons. This feature is not observed in the  $^1\text{H}$  NMR spectrum of the 1:1 complex of  $\text{Ag}^{\text{I}}$  with  $\text{L}^4$ , where only one very broad signal was recorded, or in the spectrum of the 1:1 complex of  $\text{Zn}^{\text{II}}$  with  $\text{L}^4$ , where the two observed multiplets integrate for two and six protons, respectively. The 1:1 complex of  $\text{Pb}^{\text{II}}$  with  $\text{L}^4$  presents instead three distinct groups of signals for the ethylenic fragments, two integrating for two protons each, and one for four protons. Interestingly, for the 1:1 complex of  $\text{Pb}^{\text{II}}$  with  $\text{L}^7$  four distinct multiplets are observed in the  $^1\text{H}$  NMR spectrum for the same aliphatic fragments with each integrating as two protons. As far as the methylenic protons close to the phenanthroline moiety are concerned, the 1:1 complexes of  $\text{Zn}^{\text{II}}$ ,  $\text{Cd}^{\text{II}}$ , and  $\text{Ag}^{\text{I}}$  with  $\text{L}^4$ , and the 1:1 complex of  $\text{Ag}^{\text{I}}$  with  $\text{L}^7$  show only one singlet, integrating as four protons, in the  $^1\text{H}$  NMR spectra recorded in  $\text{CD}_3\text{CN}$  at 25 °C. The complexes of  $\text{Pb}^{\text{II}}$  and  $\text{Hg}^{\text{II}}$  with  $\text{L}^4$ ,  $\text{Zn}^{\text{II}}$ ,  $\text{Pb}^{\text{II}}$ , and  $\text{Hg}^{\text{II}}$  with  $\text{L}^7$  show an AB subspectrum for the methylenic protons adjacent to the aromatic moiety, suggesting that they assume inequivalent dispositions (above and below the plane of the phenanthroline moiety) as a consequence of complexation.

All these features have already been observed in the  $^1\text{H}$  NMR spectra recorded in  $\text{CD}_3\text{CN}$  at 25 °C for the 1:1 complexes of  $\text{Pd}^{\text{II}}$ ,  $\text{Pt}^{\text{II}}$ ,  $\text{Rh}^{\text{III}}$ , and  $\text{Ru}^{\text{II}}$  with  $\text{L}^1$  and  $\text{L}^2$  isolated in the solid state.<sup>39</sup> Unfortunately, for solubility reasons, it was not possible to record  $^1\text{H}$  NMR spectra in  $\text{CD}_3\text{CN}$  at different temperatures for the complexes with  $\text{L}^4$  and  $\text{L}^7$  isolated in the solid state.

**Crystal Structures of  $[\text{Cd}(\text{NO}_3)_2(\text{L}^5)]$ ,  $[\text{Pb}(\text{L}^7)](\text{ClO}_4)_2 \cdot \frac{1}{2}\text{MeCN}$ ,  $[\text{Pb}(\text{L}^4)](\text{ClO}_4)_2 \cdot \text{MeCN}$ , and  $[\text{Cu}(\text{L}^7)](\text{ClO}_4)_2 \cdot \frac{3}{2}\text{MeNO}_2$ .** The complexation ability of  $\text{L}^1$ – $\text{L}^3$  (the most studied among the ligands shown in Figure 1) toward many transition and post-transition metal ions in the solid state has been already widely investigated. It is mainly 1:1 metal complexes that have been isolated and structurally characterized:<sup>39–42,44</sup> in these, the ligands commonly adopt a folded conformation, with the aliphatic chain of the ring tilted over the plane containing the phenanthroline unit, while attempting to encapsulate (in the cases of  $\text{L}^1$  and  $\text{L}^2$ ) the metal ions in a square-based pyramidal stereochemistry within their cavity. Depending on the stereoelectronic requirements of the metal ions considered, *pseudo*-octahedral or square-based pyramidal coordinations can be achieved by interaction of counteranions or solvent molecules at the coordination sites not occupied by the donor atoms of the macrocycles. The



**Figure 5.** View of  $[\text{Cd}(\text{NO}_3)_2(\text{L}^5)]$  with the numbering scheme adopted. Hydrogen atoms are omitted for clarity.

structure of the  $\text{Cu}^{\text{I}}$  complex  $[\text{Cu}(\text{L}^1)(\text{Cl})(\text{PPh}_3)]^{44}$  is quite remarkable in that none of the S-donors in the aliphatic chain of the macrocycle is coordinated to the metal center. A distorted tetrahedral coordination sphere at the  $\text{Cu}^{\text{I}}$  center is achieved via the two N-donors of  $\text{L}^1$ , a chloride ligand, and a  $\text{PPh}_3$  ligand. On the other hand, only one complex with a 1:2 metal to ligand stoichiometry has been crystallographically characterized:  $[\text{Pb}(\text{L}^3)_2](\text{ClO}_4)_2 \cdot 2\text{MeCN}^{42}$  features the metal center sandwiched between two symmetry-related molecules of  $\text{L}^3$  with an overall  $[4\text{N} + 4\text{S}]$  eight-coordination.

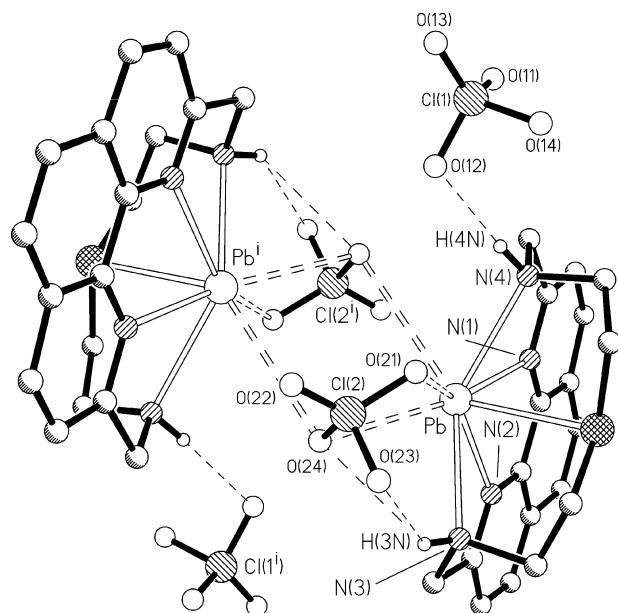
With  $\text{L}^4$  and  $\text{L}^7$ , 1:1 metal complexes of  $\text{Cu}^{\text{II}}$ ,  $\text{Zn}^{\text{II}}$ ,  $\text{Cd}^{\text{II}}$ ,  $\text{Pb}^{\text{II}}$ ,  $\text{Hg}^{\text{II}}$ , and  $\text{Ag}^{\text{I}}$  were isolated in the solid state (see Supporting Information); crystals suitable for X-ray structural analysis were only obtained for the complexes  $[\text{Pb}(\text{L}^7)](\text{ClO}_4)_2 \cdot \frac{1}{2}\text{MeCN}$ ,  $[\text{Pb}(\text{L}^4)](\text{ClO}_4)_2 \cdot \text{MeCN}$ , and  $[\text{Cu}(\text{L}^7)](\text{ClO}_4)_2 \cdot \frac{3}{2}\text{MeNO}_2$ . We also report here the crystal structure of  $[\text{Cd}(\text{NO}_3)_2(\text{L}^5)]$ , only the second example of a complex with  $\text{L}^5$  to be structurally characterized, the first being  $[\text{Ag}(\text{L}^5)]\text{BF}_4^{45}$ .

In  $[\text{Cd}(\text{NO}_3)_2(\text{L}^5)]$  an overall  $\text{N}_3\text{S}_2\text{O}_3$  eight-coordination is apparently achieved at the metal center via the five donor atoms of the macrocyclic ligand and three O-donors, deriving respectively from one terminal asymmetrical bidentate and one monodentate  $\text{NO}_3^-$  ion (Figure 5, Table 3). The metal center is slightly displaced by  $0.33 \text{ \AA}$  out of the mean plane defined by the atoms N(1), N(2), S(1), and S(2) toward the  $\text{NO}_3^-$  ligands. The coordination environment can be described as monocapped *pseudo*-octahedral if the asymmetrical bidentate nitrate ligand is considered to formally occupy the apical position of a *pseudo*-octahedron, the other being occupied by the tertiary amino group [N(3)] from  $\text{L}^5$ . The conformation adopted by  $\text{L}^5$  in this complex is very similar to that observed in the square-pyramidal complex cation  $[\text{Ag}(\text{L}^5)]^{+45}$  and characteristic of other macrocycles of this type having the aliphatic portion of the ring folded over the phenanthroline unit. Bond distances are comparable to those observed in the complex  $[\text{Cd}(\text{NO}_3)_2(\text{L}^3)]^{42}$  in which, however, only the two S-donors are present in the aliphatic portion of the ring, and the two nitrate groups are almost

**Table 3.** Selected Bond Distances ( $\text{\AA}$ ) and Angles (deg) for  $[\text{Cd}(\text{NO}_3)_2(\text{L}^5)]^a$

Cd—N(1)	2.411(6)	Cd—S(2)	2.726(4)
Cd—N(2)	2.455(6)	Cd—O(1)	2.478(8)
Cd—N(3)	2.540(9)	Cd—O(4)	2.431(9)
Cd—S(1)	2.696(3)	Cd—O(5)	2.725(11)
N(1)—Cd—N(2)	68.7(2)	N(2)—Cd—O(4)	75.4(2) [107.5(4)]
N(1)—Cd—N(3)	93.5(3)	N(3)—Cd—S(1)	77.0(2)
N(1)—Cd—S(1)	72.6(2)	N(3)—Cd—S(2)	76.1(2)
N(1)—Cd—S(2)	139.4(2)	N(3)—Cd—O(1)	110.7(3)
N(1)—Cd—O(1)	140.7(2)	N(3)—Cd—O(4)	161.3(3) [150.0(4)]
N(1)—Cd—O(4)	92.3(3) [71.9(4)]	S(1)—Cd—S(2)	138.9(1)
N(2)—Cd—N(3)	90.3(2)	S(1)—Cd—O(1)	83.0(2)
N(2)—Cd—S(1)	138.3(2)	S(1)—Cd—O(4)	121.7(2) [73.7(4)]
N(2)—Cd—S(2)	72.2(2)	O(1)—Cd—O(4)	74.7(3) [71.9(4)]
N(2)—Cd—O(1)	138.1(3)	O(4)—Cd—O(5)	48.32(1)

<sup>a</sup> Where two values are reported, the first refers to the bond distances and angles involving O(4), and the second to the bond distances and angles involving O(5) (Figure 3).



**Figure 6.** View of the dimeric units in  $[\text{Pb}(\text{L}^7)](\text{ClO}_4)_2 \cdot \frac{1}{2}\text{MeCN}$  with the adopted numbering scheme. Hydrogen atoms, except those on the secondary amino groups are omitted for clarity.  $\text{H}(3\text{N}) \cdots \text{O}(23)$   $3.36(2) \text{ \AA}$ ,  $\text{N}(3) - \text{H}(3\text{N}) \cdots \text{O}(23)$   $143.1(7)^\circ$ ;  $\text{H}(3\text{N}) \cdots \text{O}(24)$   $2.60(1)$ ,  $\text{N}(3) \cdots \text{O}(24)$   $3.19(1) \text{ \AA}$ ,  $\text{N}(3) - \text{H}(3\text{N}) \cdots \text{O}(24)$   $123.9(6)^\circ$ ;  $\text{H}(4\text{N}) \cdots \text{O}(12)$   $2.25(2)$ ,  $\text{N}(4) \cdots \text{O}(12)$   $3.15(2) \text{ \AA}$ ,  $\text{N}(4) - \text{H}(4\text{N}) \cdots \text{O}(12)$   $175.9(7)^\circ$ ;  $i = \frac{3}{2} - x, \frac{3}{2} - y, 1 - z$ .

symmetrically bidentate to give a distorted cubic  $\text{N}_2\text{S}_2\text{O}_4$  environment.

In  $[\text{Pb}(\text{L}^7)](\text{ClO}_4)_2 \cdot \frac{1}{2}\text{MeCN}$  each  $[\text{Pb}(\text{L}^7)]^{2+}$  cation is arranged about a center of symmetry and forms a dimeric pair with a symmetry related counterpart via two terdentate perchlorate bridging anions, as shown in Figure 6. The bridging perchlorate ligands are anchored to the  $[\text{Pb}(\text{L}^7)]^{2+}$  cations via bifurcated H-bonds involving one of the secondary nitrogen atoms of the aliphatic portion of  $\text{L}^7$  [N(3)]. The other NH group [N(4)] is hydrogen bonded to a further perchlorate ion. The bonds to the donor atoms are evenly distributed about the  $\text{N}_4\text{SO}_3$  eight-coordination sphere but some are significantly longer than others (Table 4). In particular, the donor atoms from the macrocyclic unit are more strongly coordinated to the metal centers with distances in the ranges  $2.492(9) - 2.495(6)$ ,  $2.661(10) - 2.701(10)$ , and  $2.806(3) \text{ \AA}$  for the  $\text{Pb}-\text{N}_{\text{phen}}$ ,  $\text{Pb}-\text{N}_{\text{amino}}$ , and the  $\text{Pb}-\text{S}_{\text{thioether}}$

**Table 4.** Selected Bond Distances (Å) and Angles (deg) for [Pb(L<sup>7</sup>)](ClO<sub>4</sub>)<sub>2</sub>·<sup>1</sup>/<sub>2</sub>MeCN]

Pb–N(1)	2.495(6)	Pb–S	2.806(3)
Pb–N(2)	2.492(9)	Pb–O21	3.062(11)
Pb–N(3)	2.701(10)	Pb–O24	3.190(8)
Pb–N(4)	2.661(11)	Pb <sup>i</sup> –O24	3.358(9)
N(1)–Pb–N(2)	65.2(3)	N(3)–Pb–N(4)	137.6(3)
N(1)–Pb–N(3)	122.3(2)	N(3)–Pb–S	70.5(2)
N(1)–Pb–N(4)	64.8(3)	N(4)–Pb–S	69.9(2)
N(1)–Pb–S	80.7(2)	S–Pb–O(21)	81.7(1)
N(2)–Pb–N(3)	62.1(3)	S–Pb–O(24)	113.5(1)
N(2)–Pb–N(4)	125.6(3)	Pb–O(24)–Pb <sup>i</sup>	95.0(1)
N(2)–Pb–S	82.1(2)		

$$^i = {}^3/2 - x, {}^3/2 - y, 1 - z.$$

bonds, respectively. The O-donors of the perchlorate ions are at rather longer distances, ranging from 3.062(11) [Pb–O(21)] to 3.358(9) Å [Pb<sup>i</sup>–O(24)] (Figure 6, Table 4) and, being significantly longer than those normally found for O-donating counter-anions coordinated to lead(II), they are better considered as long contacts.<sup>42</sup> In fact, they are also longer than the sum of the Shannon ionic radius of eight-coordinate lead(II) (1.29 Å)<sup>69</sup> and the van der Waals radius of oxygen (1.50 Å).<sup>70</sup> This structural feature might be indicative of the presence of a stereochemically active 6s<sup>2</sup> lone pair positioned in the coordination hemisphere left free by the macrocyclic ligand. In [Pb(L<sup>7</sup>)]<sup>2+</sup> the metal center is “perching” above the macrocyclic cavity of L<sup>7</sup>, which assumes the usual folded conformation, rather than “nesting” within it, and is displaced 0.60 Å out of the mean plane defined by the atoms N(1), N(2), N(3), and N(4) toward the O-donor manifold of the perchlorate anions. The structural features of each binuclear system in [Pb(L<sup>7</sup>)](ClO<sub>4</sub>)<sub>2</sub>·<sup>1</sup>/<sub>2</sub>MeCN are reminiscent of those observed in [Pb(L<sup>1</sup>)](ClO<sub>4</sub>)<sub>2</sub>·<sup>1</sup>/<sub>2</sub>H<sub>2</sub>O in which two bidentate perchlorate ions and a water molecule bridge two symmetry related [Pb(L<sup>1</sup>)]<sup>2+</sup> units and the metal center achieves overall nine-coordination via a further perchlorate ion acting as monodentate ligand.<sup>42</sup>

On passing from L<sup>7</sup> to L<sup>4</sup> a mononuclear lead(II) complex is obtained. In [Pb(L<sup>4</sup>)](ClO<sub>4</sub>)<sub>2</sub>·MeCN two independent [Pb(L<sup>4</sup>)]<sup>2+</sup> cations are present in the asymmetric unit. In each cation the metal center interacts with an acetonitrile molecule and two perchlorate ligands in the hemisphere left free by the N<sub>3</sub>S<sub>2</sub>-donating macrocyclic ligand. Unfortunately, because of severe disorder, the positions of the perchlorate oxygen atoms can only be considered approximate and probably do not describe the full range of anion orientations. Consequently, we feel the exact coordination number achieved at the metal center cannot be given (Figure S4 in the Supporting Information). A similar mononuclear lead(II) complex is obtained with the pentadentate L<sup>2</sup> in [Pb(L<sup>2</sup>)](ClO<sub>4</sub>)<sub>2</sub>·MeNO<sub>2</sub>; in this case nine-coordination is achieved at the metal center via a nitromethane molecule and one terminal bidentate and one monodentate ClO<sub>4</sub><sup>−</sup> ion.<sup>42</sup>

Two independent complex units (A and B) are present in the asymmetric unit of [Cu(L<sup>7</sup>)](ClO<sub>4</sub>)<sub>2</sub>·<sup>3</sup>/<sub>2</sub>MeNO<sub>2</sub>. In unit A (Figure 7a, Table 5), an overall *pseudo*-octahedral

coordination sphere is achieved at the Cu(II) center, similar to that observed in the cation [Cu(L<sup>2</sup>)(ClO<sub>4</sub>)]<sup>+</sup>,<sup>44</sup> by interaction of a monodentate perchlorate ligand at the coordination site left free by the macrocyclic ligand, which acts as a pentadentate N<sub>4</sub>S-donor by assuming the usual folded conformation. In unit B (Figure 7b, Table 5), no interaction of a perchlorate ligand with the metal ion is observed, which, therefore, lies within a distorted square-based pyramidal coordination environment imposed by the macrocyclic ligand. Pairs of [Cu(B)(L<sup>7</sup>)]<sup>2+</sup> cations related by crystallographic inversion centers interact with each other via S⋯S contacts of 3.529(2) Å (Figure 7c). The resulting dimers interact with two adjacent cations [Cu(A)(L<sup>7</sup>)(ClO<sub>4</sub>)]<sup>+</sup> via weak π-π interactions of about 3.5 Å between the phenanthroline moieties to give the tetramers shown in Figure 7c. An intricate network of H-bonds involving these tetramers, perchlorate ligands, and MeNO<sub>2</sub> molecules contribute to the crystal packing. Examples of hydrogen bonding involving metal complex units and perchlorate anions are shown in Figures S5–S7 in the Supporting Information.

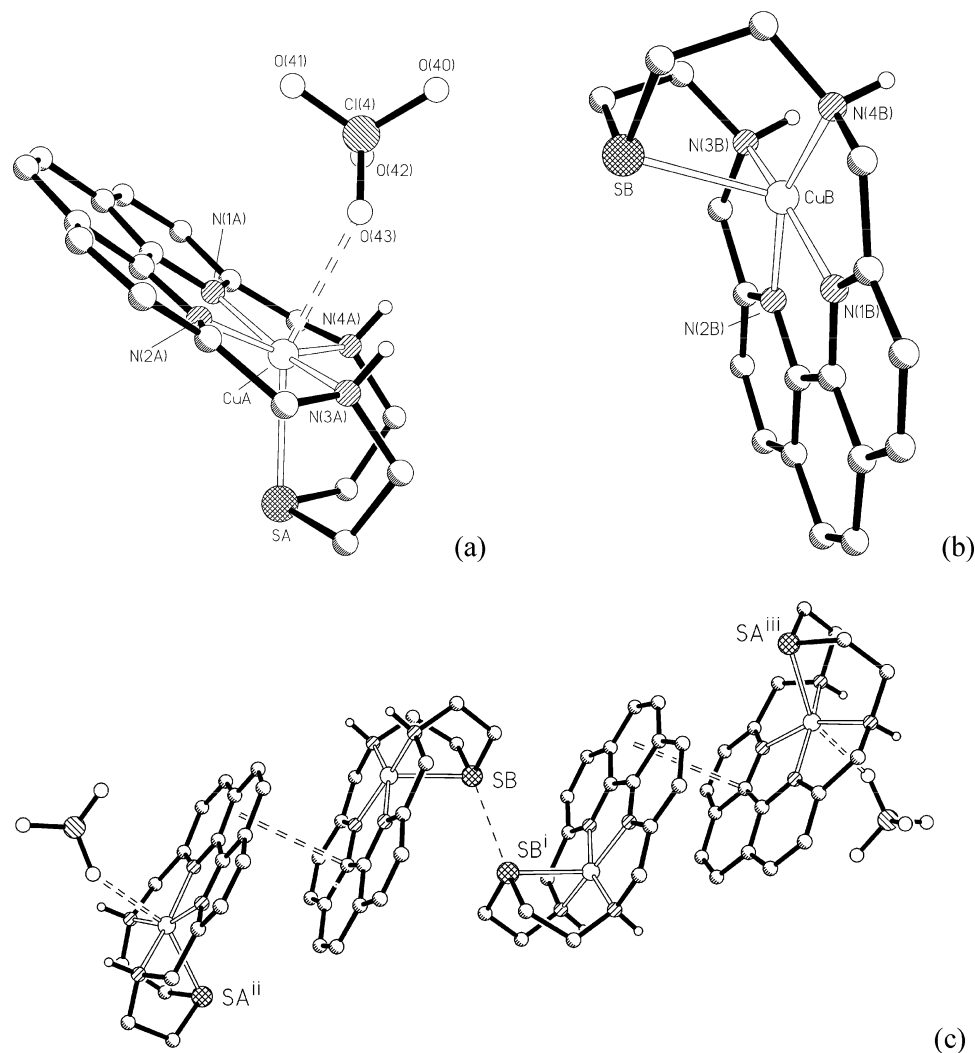
**Liquid–Liquid Extraction Studies.** The macrocyclic ligands L<sup>1</sup>–L<sup>7</sup> were tested as extractants for liquid–liquid extraction of a series of metal ions showing typical borderline (Cu<sup>II</sup>, Zn<sup>II</sup>) or soft (Ag<sup>I</sup>, Cd<sup>II</sup>, Hg<sup>II</sup>, Pb<sup>II</sup>) acid character. The aim of the studies was to verify the effects of the different donor atoms within the macrocyclic ligands on the metal ion recognition process under the experimental conditions determined by this technique. The solvent extraction studies for L<sup>7</sup> were unsuccessful because of the formation of precipitate at the aqueous/organic interfaces in all experiments performed. This behavior could be related to a high water solubility of L<sup>7</sup> as compared to that of the other ligands. Another experimental problem was related to the Hg<sup>II</sup> determination using the ICP-OES technique. In most cases the inconsistent intensity changes of the three specific Hg-emission lines prevented the reproducible determination of the concentration of Hg<sup>II</sup>, obviously caused by matrix effects. Only in the case of L<sup>3</sup> were reproducible measurements possible, and a high extraction yield (>60% Hg<sup>II</sup>) has been observed under the applied experimental conditions.

Figure 8 shows a summary of the extraction behavior of L<sup>1</sup>–L<sup>6</sup> toward Ag<sup>I</sup>, Cu<sup>II</sup>, and Zn<sup>II</sup> in single ion experiments under comparable experimental conditions. A decrease in the extraction efficiency of L<sup>1</sup>–L<sup>6</sup> is observed in the order Ag<sup>I</sup> > Cu<sup>II</sup> > Zn<sup>II</sup>. All ligands show a nearly quantitative Ag<sup>I</sup> extraction (97–99%) under the experimental conditions used; in this respect, it appears that the different donor sets in the macrocyclic frameworks of L<sup>1</sup>–L<sup>6</sup> do not exert any detectable influence. In the case of the extraction of Cu<sup>II</sup>, a significant influence from the donor set of the ligands is observed instead. The Cu<sup>II</sup> extraction increases in the ligand order L<sup>2</sup> < L<sup>4</sup> < L<sup>1</sup> < L<sup>5</sup> < L<sup>3</sup> < L<sup>6</sup>. As compared to L<sup>3</sup> [47% Cu<sup>II</sup> extraction], the presence of an additional donor atom in the aliphatic portion of the macrocyclic ligand causes a decrease in the Cu<sup>II</sup> extraction power in the order tertiary amine (L<sup>5</sup>, 40%) > sulfur (L<sup>1</sup>, 17%) > secondary amine (L<sup>4</sup>, 10%) > oxygen (L<sup>2</sup>, 7%). Interestingly, the introduction of a pyridine subunit in the macrocyclic framework causes

(69) Shannon, R. D. *Acta Crystallogr., Sect A* **1976**, *32*, 751.

(70) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960.





**Figure 7.** (a) View of the independent  $[\text{Cu}(\text{L}7)(\text{ClO}_4)]^+$  cation (unit **A**) in  $[\text{Cu}(\text{L}7)](\text{ClO}_4)_2 \cdot 3/2\text{MeNO}_2$  with the atomic numbering scheme adopted; (b) view of the  $[\text{Cu}(\text{L}7)]^{2+}$  cation (unit **B**) in  $[\text{Cu}(\text{L}7)](\text{ClO}_4)_2 \cdot 3/2\text{MeNO}_2$  with the atomic numbering scheme adopted; (c) partial view of the packing diagram in  $[\text{Cu}(\text{L}7)](\text{ClO}_4)_2 \cdot 3/2\text{MeCN}$  showing dimers of  $[\text{Cu}(\text{B})(\text{L}7)]^{2+}$  interacting via  $\pi \cdots \pi$  stacking with  $[\text{Cu}(\text{A})(\text{L}7)(\text{ClO}_4)_2]^+$  cations. Hydrogen atoms, perchlorate anions, and nitromethane molecules are omitted for clarity;  $i = 1 - x, 1 - y, -z$ ;  $ii = x, 1 + y, z$ ;  $iii = -x, 1 - y, -z$ .

**Table 5.** Selected Bond Distances (Å) and Angles (deg) for  $[\text{Cu}(\text{L}7)](\text{ClO}_4)_2 \cdot 3/2\text{MeNO}_2^a$

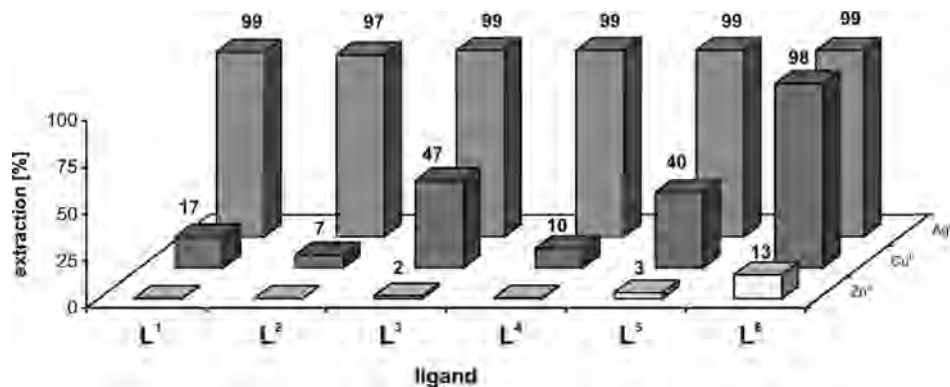
CuA—N(1A)	1.946(3) [1.939(3)]	CuA—N(4A)	2.088(4) [2.076(3)]
CuA—N(2A)	1.949(3) [1.935(3)]	CuA—SA	2.522(1) [2.505(1)]
CuA—N(3A)	2.067(4) [2.084(3)]	CuA—O(43)	2.649(1)
N(1A)—CuA—N(2A)	80.5(2) [81.2(1)]	N(2A)—CuA—O(43)	84.0(1)
N(1A)—CuA—N(3A)	157.5(2) [159.6(1)]	N(3A)—CuA—N(4A)	117.2 (2) [117.7(1)]
N(1A)—CuA—N(4A)	79.5(2) [79.4 (1)]	N(3A)—CuA—SA	84.7 (1) [86.4(1)]
N(1A)—CuA—SA	113.2(1) [107.1(1)]	N(3A)—CuA—O(43)	79.4(1)
N(1A)—CuA—O(43)	88.0(1)	N(4A)—CuA—SA	84.5(1) [85.5(1)]
N(2A)—CuA—N(3A)	79.7(2) [79.9(1)]	N(4A)—CuA—O(43)	84.2(1)
N(2A)—CuA—N(4A)	157.1(2) [158.6(1)]	SA—CuA—O(43)	153.7(1)
N(2A)—CuA—SA	113.7(1) [108.9(1)]		

<sup>a</sup> Where two values are reported, the first refers to the bond distances and angles in the independent unit **A**, and the second to the bond distances and angles in the independent unit **B** (Figure 5).

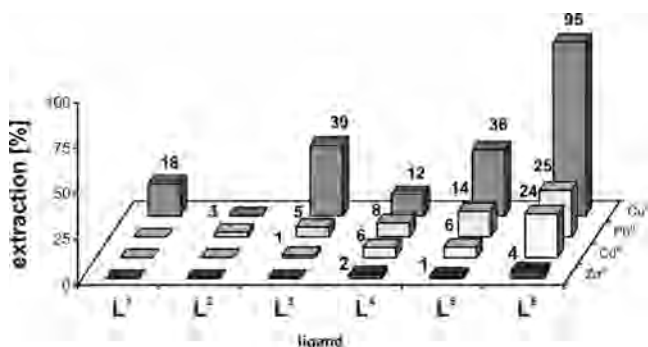
an enhancement of the  $\text{Cu}^{\text{II}}$  extraction up to 98% (**L**<sup>6</sup>, see Figure 8). In the case of the extraction of  $\text{Zn}^{\text{II}}$ , only **L**<sup>6</sup> shows a significant ability to transfer this metal ion from the aqueous to the organic phase (13%).

To investigate the extraction ability of **L**<sup>1</sup>–**L**<sup>6</sup> toward dipositive metal ions more in detail, competitive extraction experiments from an equimolar mixture of  $\text{Cu}^{\text{II}}$ ,  $\text{Zn}^{\text{II}}$ ,  $\text{Cd}^{\text{II}}$ , and  $\text{Pb}^{\text{II}}$  ions (each  $1 \times 10^{-4}$  M in water, ligands  $1 \times 10^{-3}$  M in  $\text{CHCl}_3$ ) were also carried out. Such experiments allow

us to study the selectivity of the extraction system and to establish the mutual influence of the species in solution. According to single metal ion extraction experiments, **L**<sup>1</sup>–**L**<sup>6</sup> show a pronounced affinity for  $\text{Cu}^{\text{II}}$  whereas  $\text{Pb}^{\text{II}}$ ,  $\text{Cd}^{\text{II}}$ , and  $\text{Zn}^{\text{II}}$  are only slightly extracted following the order  $\text{Pb}^{\text{II}} > \text{Cd}^{\text{II}} > \text{Zn}^{\text{II}}$  (Figure 9). The observed  $\text{Cu}^{\text{II}}$  extraction for **L**<sup>1</sup>, **L**<sup>3</sup>–**L**<sup>6</sup> in competitive experiments is very similar to the measured extraction in the single metal ion investigation (Figure 8). The results obtained for  $\text{Cd}^{\text{II}}$  and  $\text{Pb}^{\text{II}}$  indicate



**Figure 8.** Extraction of Zn<sup>II</sup>, Cu<sup>II</sup>, and Ag<sup>I</sup> by L<sup>1</sup>-L<sup>6</sup>. [M<sup>n+</sup>] = 1 × 10<sup>-4</sup> M, [NaClO<sub>4</sub>] = 5 × 10<sup>-3</sup> M, pH 6.1 (MES/NaOH buffer); [L] = 1 × 10<sup>-3</sup> M in CHCl<sub>3</sub>; shaking time 30 min; T = 21 ± 1 °C.

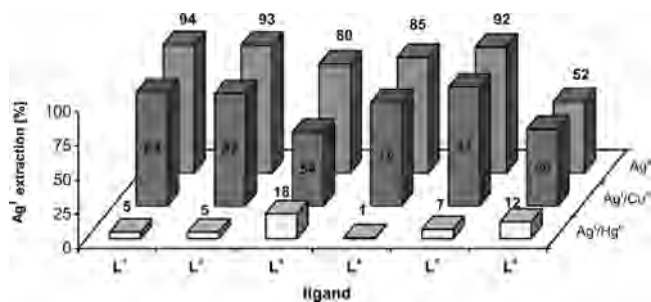


**Figure 9.** Competitive extraction of Zn<sup>II</sup>, Cd<sup>II</sup>, Cu<sup>II</sup>, and Pb<sup>II</sup> from their mixtures by L<sup>1</sup>-L<sup>6</sup>. [M<sup>n+</sup>] = 1 × 10<sup>-4</sup> M, [NaClO<sub>4</sub>] = 5 × 10<sup>-3</sup> M, pH 6.1 (MES/NaOH buffer); [L] = 1 × 10<sup>-3</sup> M in CHCl<sub>3</sub>; shaking time 30 min; T = 21 ± 1 °C.

that a nitrogen donor atom in the aliphatic portion of the ring (either as an amine group or a pyridine subunit) helps to achieve a reasonable extraction of these metals. The highest extraction of 24% (Cd<sup>II</sup>) and 25% (Pb<sup>II</sup>) is achieved with the pyridyl containing ligand L<sup>6</sup> (Figure 9). By analogy with the single metal ion extraction experiments, all ligands show only a low affinity for Zn<sup>II</sup>.

To probe the metal ion selectivity in more detail and to find discrimination factors for metal ion pairs which are chemically similar (Ag<sup>I</sup>/Hg<sup>II</sup>) or industrially important (Ag<sup>I</sup>/Cu<sup>II</sup>), competitive extraction experiments were also carried out using aqueous solutions containing equimolar concentrations of these metal ions (1 × 10<sup>-4</sup> M in water) and CHCl<sub>3</sub> solutions of the ligands (1 × 10<sup>-4</sup> M in CHCl<sub>3</sub>).<sup>71</sup> The distribution of Ag<sup>I</sup> between the two phases was assessed radiometrically by  $\gamma$ -radiation of <sup>110m</sup>Ag in a NaI (TI) scintillation counter (Cobra II/Canberra-Packard).<sup>59</sup> A pH value of 3.1 was chosen for the water solutions to decrease the Ag<sup>I</sup> extraction to reasonable values. Figure 10 shows the results obtained in these competitive extraction experiments together with the results obtained for single ion extraction of Ag<sup>I</sup> under comparable conditions.

Generally, in comparison with the results in Figure 8, a significant decrease of the Ag<sup>I</sup> extraction is observed, especially in the case of L<sup>6</sup>, caused by the lower pH (3.1 vs 6.1) and the lower ligand concentration (1 × 10<sup>-4</sup> M vs 1 ×



**Figure 10.** Percentage extraction of Ag<sup>I</sup> alone by L<sup>1</sup>-L<sup>6</sup> and in the presence of Hg<sup>II</sup> and Cu<sup>II</sup>. [M<sup>n+</sup>] = 1 × 10<sup>-4</sup> M, [NaClO<sub>4</sub>] = 5 × 10<sup>-3</sup> M, pH 3.1 (citric acid/NaOH buffer); [L] = 1 × 10<sup>-4</sup> M in CHCl<sub>3</sub>; shaking time 30 min; T = 21 ± 1 °C.

10<sup>-3</sup> M) according to the following graded extraction order for Ag<sup>I</sup>: L<sup>1</sup> ~ L<sup>2</sup> ~ L<sup>5</sup> > L<sup>4</sup> > L<sup>3</sup> > L<sup>6</sup>. The presence of Cu<sup>II</sup> and especially of Hg<sup>II</sup> causes a further decrease of the Ag<sup>I</sup> extraction which suggests a strong mutual influence on the extraction of these metal ions. However, the extraction of Ag<sup>I</sup> is still favored in the presence of Cu<sup>II</sup> but not in the presence of Hg<sup>II</sup>. In the case of the metal ion pair Ag<sup>I</sup>/Hg<sup>II</sup> the significantly lower extraction power for Ag<sup>I</sup> suggests that the binding and extraction of Hg<sup>II</sup> is favored. All this could represent valuable information relevant to technologies for the separation and purification of silver. The silver content of environmental samples is drastically increasing because of the increasing use of silver compounds and silver-containing preparations in industry and medicine. The use of artificial membranes containing neutral ionophores in Ag<sup>I</sup>-specific separation procedures often suffers from problems such as interference from some transition and heavy metal ions, partial bleeding of the ionophore in the aqueous phases, and long transport time.<sup>50,51</sup>

The extraction results shown in Figure 10 point to effective separation possibilities for Ag<sup>I</sup> over Cu<sup>II</sup> with the ligands L<sup>1</sup>, L<sup>2</sup>, L<sup>4</sup>, and L<sup>5</sup>. Furthermore, these data indicate that not only L<sup>4</sup> but also L<sup>1</sup> and L<sup>2</sup> could possibly be considered as good candidate ionophores for the selective extraction of Hg<sup>II</sup>, a toxic element of particular environmental concern, from water solutions in the presence of Ag<sup>I</sup>.

## Conclusions

This manuscript describes the results achieved by a wide-ranging study concerned with metal ion recognition using

(71) Wu, G.; Jiang, W.; Lamb, J. D.; Bradshaw, J. S.; Izatt, R. M. *J. Am. Chem. Soc.* **1991**, *113*, 6538.

phenanthroline containing macrocyclic ligands and employing different conditions and techniques. Apart from the intrinsic interest in the coordination chemistry of the ligands presented, the study demonstrates that results can vary with both the latter in particular instances, and hence, the observed behavior does not necessarily reflect the intrinsic metal ion affinity inherent in the design of a given macrocycle. While this has been recognized for some time, we reckon the message is worth reinforcing. Macrocyclic-based molecular systems often do not accomplish properly the role of the specific ionophore for which they were initially designed, and it is therefore essential to test their ability as receptors in molecular recognition processes in different chemical situations and employing different techniques for different analytical purposes.

**Acknowledgment.** We thank the “Regione Autonoma della Sardegna”, the Università degli Studi di Cagliari, and the Deutsche Forschungsgemeinschaft for financial support.

**Supporting Information Available:** Synthetic details including analytical data for the isolated 1:1 metal complexes of  $L^4$  and  $L^7$ . Stepwise Formation Constants of  $Pb^{II}$ ,  $Cd^{II}$ ,  $Hg^{II}$ ,  $Cu^{II}$  with  $L^1$ - $L^3$  and of  $Ag^I$  with  $L^1$ - $L^3$ , and  $L^5$  in MeCN at 25 °C, calculated by fitting the Fluorescence/Molar Ratio data (Table S1);  $^1H$  chemical shifts ( $\Delta\delta$ , ppm) of  $L^4$  and  $L^7$  observed in the presence of 1 equiv of metal ions in  $CD_3CN/H_2O$  4:1 (v/v) mixtures (pD = 7.0) at 25 °C (Table S2); distribution diagrams for the systems  $H^+/L^4$  (a),  $Cu^{II}/L^4$  (b) and  $Cd^{II}/L^4$  (c) in water 0.1 M  $NMe_4NO_3$  (Figure S1); distribution diagrams for the systems  $Cu^{II}/L^7$  (a) and  $Pb^{II}/L^7$  (b) in water 0.1 M  $NMe_4NO_3$  (Figure S2); distribution diagrams for the systems  $Hg^{II}/L^4$  (a) and  $Hg^{II}/L^7$  (b) 0.1 M  $NMe_4Cl$  water solutions (Figure S3); views of the two independent  $[Pb(L^4)]^{2+}$  complex cationic units in  $[Pb(L^4)](ClO_4)_2 \cdot MeCN$  (Figure S4); partial views of selected features of the H-bonding network in  $[Cu(L^7)](ClO_4)_2 \cdot 3/2 MeNO_2$  (Figures S5, S6, S7); crystallographic data in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

IC800548P