Article

J. Mex. Chem. Soc. **2007**, *51(1)*, 27-32

ISSN 1870-249X

Mono and Dinuclear Cadmium(II) Complexes with the Ligand *cis*-2,4,5-tri(2-pyridyl)imidazoline

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Recibido el 12 de septiembre del 2006; aceptado el 13 de diciembre del 2006

Resumen. El ligando polipiridínico *cis*-2,4,5-tri(2-piridil)imidazolina (**L**) forma complejos de Cd(II) con diferente nuclearidad, [Cd(L)$(NO_3)_2$(MeOH)] (**1**) y [Cd(μ-L)Cl_2]$_2$ (**2**), comportándose de manera tridentada. La estructura de **1** muestra un complejo mononuclear, mientras que la de **2** consiste de un complejo dinuclear con **L** como puente entre dos centros metálicos. En **1** se observan enlaces de hidrógeno intramoleculares e intermoleculares formando cadenas 1-D, así como una interacción del tipo CH···π. En la estructura del complejo **2** se observa sólo una interacción del tipo π-π intramolecular.
Palabras clave: Ligando polipiridínico, imidazolina, Cadmio(II), Estructura cristalina, Complejo mononuclear, Complejo dinuclear, Interacciones no-covalentes.

Abstract. The polypyridyl ligand *cis*-2,4,5-tri(2-pyridyl)imidazoline (**L**) is found to form Cd(II) complexes of different nuclearity, [Cd(L)$(NO_3)_2$(MeOH)] (**1**) and [Cd(μ-L)Cl_2]$_2$ (**2**), behaving as a tridentate ligand. The X-ray diffraction analysis of **1** shows a mononuclear complex, while the structure of **2** consists of a dinuclear complex with two **L** ligands bridging the two metal centres. Intra and intermolecular hydrogen bonds are observed in **1** forming 1-D chains, as well as one intramolecular CH···π interaction. In **2** only one intramolecular π-π interaction is observed.
Key words: Pyridyl and imidazoline ligand, Cadmium(II), Crystal structure, Mononuclear complex, Dinuclear complex, non-covalent interactions.

Introduction

Complex metal-organic coordination polymers, macrocycles, networks and other metalosupramolecular structures can be constructed by self-assembly from small, easily prepared building blocks, which are combined either through coordinative bonds, hydrogen bonding [1], π-π [2] or CH/π interactions [3]. Such supramolecular architectures have attracted considerable attention due to the useful electronic, magnetic, optical and catalytic properties of these materials [4].

The coordination chemistry of transition metals with polypyridyl ligands has progressed considerably during the last decade, and has been widely used for the construction of coordination polymers and other supramolecular structures [5]. In this respect the polypyridyl ligand *cis*-2,4,5-tri(2-pyridyl)imidazoline (**L**), whose synthesis and structure has been reported by Walsh and coworkers [6], seems to be an interesting candidate. Given the strong affinity of late transition metals for pyridine-based ligands [7], we began to explore the bonding and reactivity of **L** with M(II) ions of groups 10, 11 and 12. As suggested by the geometry of **L** (Figure 1), the ligand could coordinate in at least two different modes: (*i*) through two independent bidentate sites that are each anticipated to bind the metal in a *cis* fashion, the 2-(2-pyridyl) group and the imidazoline nitrogen comprise one binding site, and the *cis* 4- and 5-(2-pyridyl) groups form the second, and (*ii*) in a tridentate mode through the 2-(2-pyridyl) group, the imidazoline nitrogen and one *cis* 4- or 5-(2-pyridyl) group. In our initial work it was shown that *cis*-2,4,5-tri(2-pyridyl)imidazoline (**L**) readily forms dimeric complexes with Ni(II), Cu(II) and Zn(II) to give the (*cis*-2,4,5-tri(2-pyridyl)imidazoline)$_2$M$_2^{4+}$

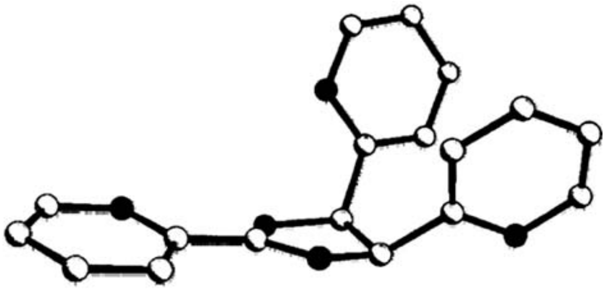


Fig. 1. Ball-and-stick drawing of the structure of **L**. The black spheres represent nitrogen atoms and the white spheres carbon atoms.

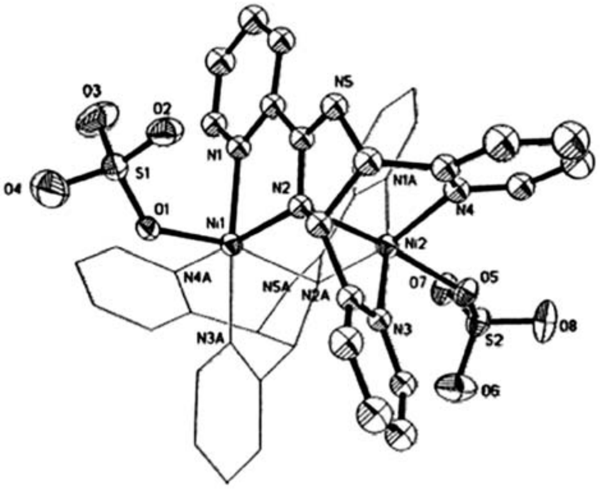


Fig. 2. Perspective view of the molecular structure of the dimer (**L**)$_2$Ni$_2$(SO$_4$)$_2$. For clarity, one ligand is drawn in an ORTEP format, while the other is illustrated as a line drawing [7].

adducts with coordination mode (*i*), as shown in Figure 2 for the Ni(II) complex [8].

As part of our continuing interest in the coordination chemistry of ligand **L**, we describe here two complexes formed between Cd(II) and **L** that display coordination mode (*ii*). An analysis on how counteranion, solvent and non-covalent interactions influence their structures, is included.

Results and Discussion

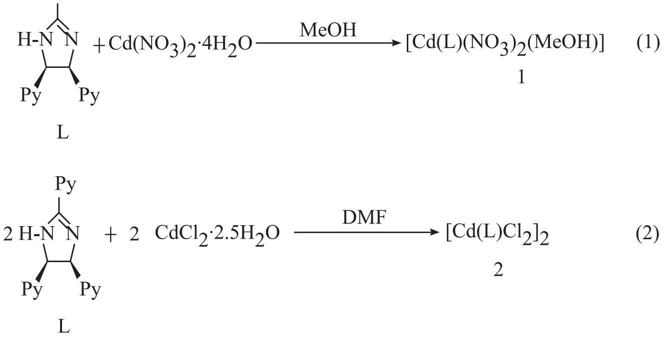
Synthesis and General Characterization

An equimolar quantity of the neutral tripyridyl ligand **L** was reacted with two different Cd(II) salts, $Cd(NO_3)_2·4H_2O$ and $CdCl_2·2.5H_2O$, to give compounds **1** and **2**, respectively. The choice of solvents for the synthesis of the complexes was dependent on the solubility of the metal precursors and ligand **L**. The ligand is soluble in organic solvents such as dichloromethane, chloroform, acetonitrile, methanol, ethanol, dimethyl formamide and dimethyl sulfoxide, but insoluble in water.

Complex **1** was prepared by combining a solution of $Cd(NO_3)_2·4H_2O$ in methanol with **L** (Equation 1). Mixing of these reagents resulted in the formation of a colorless solution. Crystallization was induced by vapor phase diffusion of diethyl ether into the reaction mixture, which provided colorless crystals of the monomer $[Cd(\mathbf{L})(NO_3)_2(MeOH)]$ (**1**) in 90% yield.

The synthesis of complex **2** was performed by adding $CdCl_2·2.5H_2O$ to a dimethylformamide (dmf) solution of **L** (Equation 2). Gas phase diffusion of diethyl ether into the resulting clear solution provided colorless crystals of the dimer $[Cd(\mu\text{-}L)Cl_2]_2·3$ DMF (**2**×3DMF) in 83% yield. This compound is insoluble in most organic solvents, except for dimethyl sulfoxide (dmso).

The infrared spectra for compounds **1** and **2** show characteristic absorption bands resulting from (i) the skeletal vibrations of the aromatic rings in the 1564-1437 cm^{-1} region, (ii) the stretching vibration of the $C{=}N_{imino}$ functions at 1584 and 1580 cm^{-1}, respectively, and (iii) the imidazoline N-H stretching vibrations in the range of 3259-3232 cm^{-1}. For **1**, characteristic bands of NO_3^- stretching appear at 1435, 1383 and 1290 cm^{-1}, consistent with a bidentate binding mode of the NO_3^- anions [9]. Finally, a broad O-H stretching band for the methanol molecule can be seen at 3259 cm^{-1}, overlapping with the imidazoline N-H stretching band. For **2**, the inclusion of dmf molecules in the crystal lattice is indicated by the presence of a supplementary absorption band at 1656 cm^{-1}.



Equations 1 and 2

The ^1H NMR spectra of compounds **1** and **2** show the amine N-H proton resonance at 9.52 and 9.31 ppm, respectively. The 12 aromatic protons of **1** gave signals in the range of 8.60-6.80 ppm, while those of **2** appear in the range of 8.63-6.92 ppm as unresolved multiplets. The two aliphatic protons of **1** and **2** at 5.81 and 5.72 ppm, respectively, gave singlets, which is in agreement with the Karplus plot [10] that predicts a coupling constant of $J \approx 0$ Hz for a H-C-C-H angle of approximately 84º. In contrast, for the free ligand a coupling constant of $J = 11.0$ Hz, according to an angle close to 0°, has been measured.

The FAB-MS spectra did not show peaks for the molecular ion of either complex; however, fragments were observed, which support the molecular composition of the complexes. In the case of complex **1** the base peak at *m/z* = 477 corresponds to the ion $[M\text{-}(NO_3)\text{-}(MeOH)]+$. For **2** there is one peak at *m/z* = 751 for the fragment $[M\text{-}CdCl_2\text{-}Cl]^+$ and the base peak at m/z = 450 corresponds to the ion $[M\text{-}2Cl]^{2+}$. These assignments have been confirmed by HR-FAB$^+$ spectrometry (see experimental section).

The molecular structures of monomer **1** and dimer **2** were determined by X-ray diffraction studies. The ORTEP diagrams are shown in Figures 3 and 5, respectively. The most relevant crystallographic data are summarized in Table 1. Selected bond lengths and angles as well as hydrogen bonding interactions are listed in Tables 2 and 3.

In contrast to previously reported complexes, in which **L** coordinates in the form of a tetradentate ligand [8], in these structures the ligand adopts a N,N,N-tridentate coordination mode.

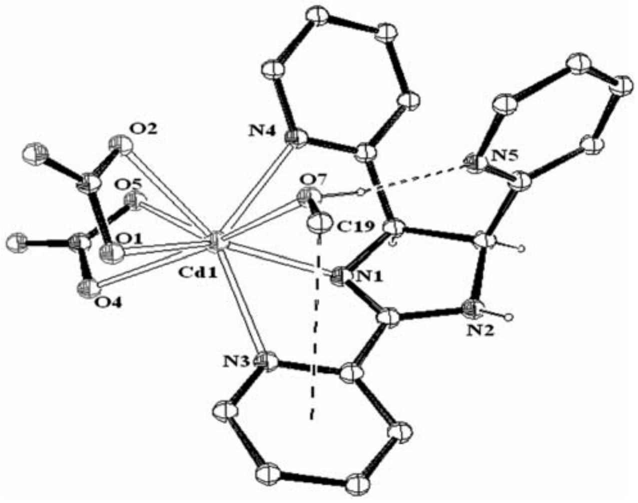


Fig. 3. Perspective view of the molecular structure of the monomeric complex $[Cd(L)(NO_3)_2(MeOH)]$ (**1**), showing the numbering scheme and the thermal ellipsoids at the 50% probability level (dashed lines indicate the H-bonding and a weak CH···π interaction).

Table 1. Crystallographic data and collection parameters for **1** and **2**.

	1	**2** ·3DMF
empirical formula	$C_{19}H_{19}CdN_7O_7$	$C_{90}H_{102}Cd_4Cl_8N_{26}O_6$
MW (g mol^{-1})	569.81	2377.18
space group	*C*2/c	*P*-1
a, Å	28.914(2)	8.6335(6)
b, Å	9.6287(7)	12.8550(8)
c, Å	15.8354(12)	23.4957(15)
á, deg	90	76.872(10)
â, deg	97.772(10)	87.093(10)
ã, deg	90	81.5470(10)
V, Å^3	4368.1(6)	2511.5(3)
Z	8	1
ρ_{calcd}(g cm^{-3})	1.733	1.572
μ, mm^{-1}	1.058	1.113
θ limits (°)	$2 < \theta < 25$	$2 < \theta < 25$
No. collected refl.	10187	11028
No. indep. refl. (R_{int})	3829 (2.14)	8132 (1.49)
No. observed refl.[a]	3415	7378
R,[b]	0.0389	0.0377
R_w[c]	0.0414	0.0955
GOF	1.076	1.050
$\Delta\rho_{max}$ (e Å^{-3})	0.52	0.89

[a] $I > 2\sigma(I)$. [b] $R = \Sigma(F_o^2 - F_c^2)/\Sigma F_o^2$. [c] $R_w = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

The molecular structure of **1** consists of one ligand and one Cd(II) centre in a monomeric composition, with the ligand coordinating in a tridentate manner through the 2-(2-pyridyl) nitrogen, the imine nitrogen and the 4-(2-pyridyl) nitrogen. The central metal atom has a coordination number of eight and displays a severely distorted square antiprismatic geometry, defined by the coordination of the three nitrogen atoms, four oxygen atoms from two bidentate nitrate groups and one oxygen from a methanol molecule. The distortion is indicated by the deviations from an ideal square antiprism having X-M-X angles of 59° [11] (51.30(8)°-151.09(10)°), and should be due to ligand bond requirements (Table 1).

In the molecular structure of **1,** two five-membered Cd-N-C-C-N and two four-membered Cd-O-N-O ring chelates are observed. The Cd-N(pyridyl) distances are found in the range of 2.477(3)-2.484(3) Å, and are larger than the Cd-N(imine) distance of 2.260(3) Å; the Cd-O distances are in the range of 2.379(3)-2.553(3) Å. Interestingly, in complex **1** an intramolecular O-H···N hydrogen bond (0.84 Å, 1.97 Å, 2.80 Å, 170.9 °) formed between the coordinated MeOH molecule and the free 2-pyridyl group is observed. In the crystal lattice the monomeric units form 1D polymeric zigzag chains (Figure 4) through intermolecular N-H···O hydrogen bonds (0.86 Å, 2.17 Å, 2.98 Å, 157.8 °) between the MeOH molecules and the imidazoline N-H hydrogens. The hydrogen bond distances are within the range found for other reported structures [12]. The Cd···Cd distances in the polymeric chain are 8.95 Å and there-

Table 2. Selected bond lengths (Å) and angles (°) for complex **1**.

Cd(1)-N(1)	2.260(3)	N(1)-C(1)	1.279(4)
N(4)-C(9)	1.336(4)	N(1)-C(3)	1.460(4)
C(3)-C(9)	1.512(5)	N(3)-C(4)	1.344(4)
Cd(1)-N(4)	2.477(3)	N(4)-C(9)	1.336(4)
Cd(1)-N(3)	2.484(3)	C(1)-C(4)	1.474(4)
Cd(1)-O(1)	2.497(3)	C(3)-C(9)	1.512(5)
Cd(1)-O(7)	2.505(2)	O(7)-C(19)	1.416(5)
Cd(1)-O(5)	2.553(3)		
N(1)-Cd(1)-O(4)	121.25(10)	N(3)-Cd(1)-O(1)	78.82(8)
N(1)-Cd(1)-O(2)	150.36(9)	N(1)-Cd(1)-O(7)	83.09(8)
O(4)-Cd(1)-O(2)	83.57(10)	O(4)-Cd(1)-O(7)	151.09(10)
N(1)-Cd(1)-N(4)	68.47(9)	O(2)-Cd(1)-O(7)	79.16(8)
O(4)-Cd(1)-N(4)	126.55(9)	N(4)-Cd(1)-O(7)	74.54(8)
O(2)-Cd(1)-N(4)	83.94(8)	N(3)-Cd(1)-O(7)	77.11(9)
N(1)-Cd(1)-N(3)	69.08(9)	O(1)-Cd(1)-O(7)	76.83(8)
O(4)-Cd(1)-N(3)	96.25(9)	N(1)-Cd(1)-O(5)	104.76(10)
O(2)-Cd(1)-N(3)	128.37(8)	O(4)-Cd(1)-O(5)	50.66(10)
N(4)-Cd(1)-N(3)	130.96(8)	O(2)-Cd(1)-O(5)	77.52(10)
N(1)-Cd(1)-O(1)	145.19(9)	N(4)-Cd(1)-O(5)	75.90(9)
O(4)-Cd(1)-O(1)	74.28(10)	N(3)-Cd(1)-O(5)	138.86(10)
O(2)-Cd(1)-O(1)	51.30(8)	O(1)-Cd(1)-O(5)	108.26(9)
N(4)-Cd(1)-O(1)	130.45(9)	O(7)-Cd(1)-O(5)	143.88(10)

Bond D-H···A	D-H (Å)	H···A (Å)	D···A (Å)	∠ D-H···A (°)
N(2)-H(2')···O(1)#1	0.85	2.17	2.980	158
O(7)-H(7')···N(5)#2	0.84	1.98	2.807	171

[a] Symmetry operators: #1 x, y, z #2 x, 1-y, -½ + z

Table 3. Selected bond lengths (Å) and angles (°) for complex **2**·3DMF.

Cd(1)-N(1)	2.290(3)	Cd(2)-Cl(6)	2.4610(13)
Cd(1)-N(3)	2.383(3)	Cd(2)-Cl(4)	2.4769(14)
Cd(1)-N(10)	2.391(3)	N(1)-C(1)	1.297(5)
Cd(1)-Cl(3)	2.4584(13)	N(3)-C(4)	1.350(5)
Cd(1)-Cl(5)	2.4782(13)	N(6)-C(19)	1.300(5)
Cd(2)-N(6)	2.287(3)	N(8)-C(22)	1.343(5)
Cd(2)-N(5)	2.399(3)	C(1)-C(4)	1.480(5)
Cd(2)-N(8)	2.436(3)	C(19)-C(22)	1.482(5)
N(1)-Cd(1)-N(3)	71.03(11)	N(6)-Cd(2)-N(5)	95.63(11)
N(1)-Cd(1)-N(10)	92.12(10)	N(6)-Cd(2)-N(8)	69.98(11)
N(3)-Cd(1)-N(10)	162.16(11)	N(5)-Cd(2)-N(8)	163.18(10)
N(1)-Cd(1)-Cl(3)	105.50(9)	N(6)-Cd(2)-Cl(6)	109.89(9)
N(3)-Cd(1)-Cl(3)	92.41(8)	N(5)-Cd(2)-Cl(6)	97.10(8)
N(10)-Cd(1)-Cl(3)	97.91(8)	N(8)-Cd(2)-Cl(6)	96.06(8)
N(1)-Cd(1)-Cl(5)	132.73(9)	N(6)-Cd(2)-Cl(4)	126.20(8)
N(3)-Cd(1)-Cl(5)	90.85(9)	N(5)-Cd(2)-Cl(4)	94.58(8)
N(10)-Cd(1)-Cl(5)	96.77(9)	N(8)-Cd(2)-Cl(4)	87.56(8)
Cl(3)-Cd(1)-Cl(5)	118.92(5)	Cl(6)-Cd(2)-Cl(4)	120.94(5)

Bond A···H-D	D-H (Å)	H···A (Å)	D···A (Å)	∠ D-H···A (°)
N(2)-H(2')···O(52)#1	0.81	2.01	2.818	173
N(7)-H(7')···O(53A)#2	0.81	1.99	2.786	169
N(7)-H(7')···O(53B)#2	0.81	2.09	2.90	171

[a] Symmetry operators: #1 -x+2,-y+1,-z+1 #2 -x+1, -y+2,-z+1.

fore shorter than those in {[Cd(μ-3,3'-pytz)$(NO_3)_2(MeOH)_2$]}$_\infty$ [3-3´-pytz = 3,6-bis(pyridin-3-yl)-1,2,4,5-tetrazine] [13]. In the molecular structure of **1** a weak intramolecular interaction of the CH···π type [12] is also observed, with a C···centroid distance of 3.82 Å (distance H···centroid 3.28 Å and <C-H···centroid 117.14 °).

The molecular structure of complex **2** (Figure 5) consists of two ligands and two Cd(II) ions forming a dimeric complex. Each ligand is coordinated through the 2-(2-pyridyl) and the imine nitrogens to one Cd(II) ion forming a five-membered ring chelate, and through the 4-(2-pyridyl) nitrogen to the second Cd(II) ion, thus forming a bridge between the two metal centres. The metal centre labelled Cd(1) has a geometry intermediate between a square pyramid and a trigonal bipyramid defined by the pyridyl nitrogens N(3) and N(10), the imine nitrogen N(1), and two chloride anions, Cl(3) and Cl(5). The geometric intermediacy is represented by a value of τ = 0.49 [15], estimated from the angles N(1)-Cd(1)-Cl(5) and N(3)-Cd(1)-N(10) with values of 132.73(9)° and 162.16(11)°,

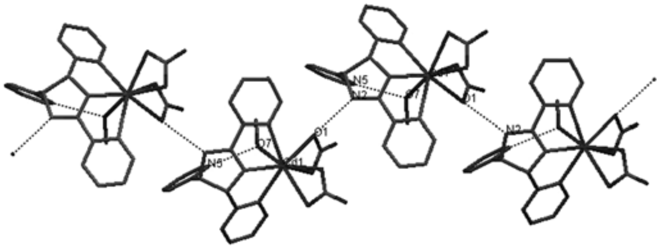


Fig. 4. View of H-bonding interactions of **1** between adjacent monomeric units to form a 1D chain (H-bonding is shown by dashed lines).

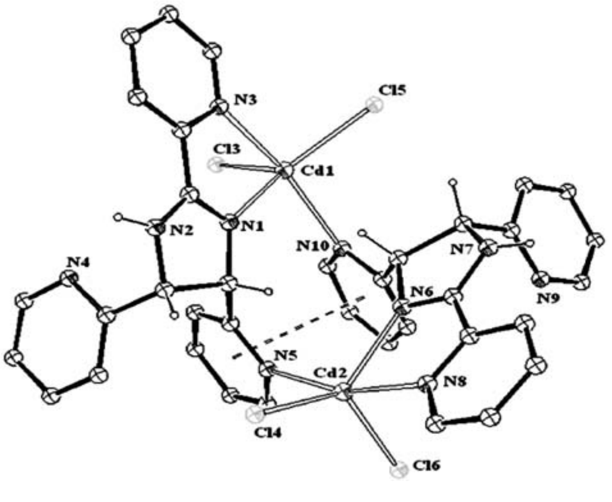


Fig. 5. Perspective view of the molecular structure of the dimeric complex $[Cd(L)(Cl)_2]_2$ (**2** ·3DMF), showing the numbering scheme and the thermal ellipsoid at the 50% probability level (dashed lines indicate the π-π interaction, solvent molecules have been omitted for clarity).

respectively. The geometry around the metal centre labelled Cd(2) is similar to that of Cd(1) and is defined by the pyridyl nitrogens N(5) and N(8), the imine nitrogen N(6), and two chloride anions, Cl(4) and Cl(6). In this case, a distortion in the direction of the trigonal bipyramidal geometry is observed as indicated by a value of $\tau = 0.61$ [15], estimated from the angles N(6)-Cd(2)-Cl(4) and N(5)-Cd(2)-N(8) with values of 126.20(8)° and 163.18(10)°, respectively, thus rendering a non-centrosymmetric structure. The Cd-N(pyridyl) distances, Cd(1)-N(3), Cd(1)-N(10), Cd(2)-N(5) and Cd(2)-N(8), are found in the range of 2.383(3)-2.436(3) Å, while the Cd-N(imine) distances, Cd(1)-N(1) and Cd(2)-N(6), are shorter, 2.290(3) Å and 2.287(3) Å, respectively. Interestingly, a strong intramolecular π-π interaction between the bridging pyridine rings is observed (Figure 5). The centroid$\cdots$centroid distance is 3.46 Å, thus being similar to those observed in related structures [16]. In the crystal lattice, intermolecular N-H$\cdots$O hydrogen bonds between the imidazoline N-H group and dmf solvate molecules are observed (Table 3).

Experimental

General

All chemicals were used as received without further purification. The synthesis and spectroscopic data for *cis*-2,4,5-tri(2-pyridyl)imidazoline (**L**) have been reported elsewhere [6]. Infrared spectra (KBr) were measured on a Perkin-Elmer 1600 series instrument. NMR spectra were recorded at 200 MHz with a Varian Mercury spectrometer at 30 °C using dmso-d_6 as the solvent and TMS as reference. FAB mass-spectrometry was carried out using a JMS-700 MSTATION. Melting points were measured on an Electrothermal GAC 88629 melting-point apparatus and are uncorrected.

Preparation of the complexes

[Cd(L)(NO_3)$_2$(MeOH)] (**1**). **L** (0.048 g, 0.162 mmol) was added as a solid to a solution of $Cd(NO_3)_2{\cdot}4H_2O$ (0.050 g, 0.162 mmol) in methanol (5 mL), and the mixture was stirred for 1 h at room temperature to give a colorless solution. The product was crystallized by gas phase diffusion of diethyl ether into the reaction mixture at room temperature providing colorless crystals, which were dried under high vacuum. Yield (0.084 g, 90% based on Cd), mp 170 °C (dec). IR (KBr): 3259, 3061, 2873, 1584, 1561, 1435, 1383, 1290 cm^{-1}. ^{1}H NMR (DMSO-d_6, 200 MHz): δ 9.52 (bs, NH, 1H), 8.60-6.80 (m, 12H), 5.81 (s, 2H). ^{13}C NMR (DMSO-d_6, 50 MHz) ä 163.8 (C^2 of imidazoline ring), 156.5 (C_5H_4N), 149.3 (C_5H_4N), 148.5 (C_5H_4N), 147.7 (C_5H_4N), 142.1 (C_5H_4N), 140.1 (C_5H_4N), 135.9 (C_5H_4N), 128.3 (C_5H_4N), 123.6 (C_5H_4N), 122.5 (C_5H_4N), 122.0 (C_5H_4N), 72.2 (C^4 of imidazoline ring), 66.7 (C^5 of imidazoline ring). MS (HR-FAB$^+$) *m/z*: 477.0197 (100%, -9.0 ppm for $C_{18}H_{15}CdN_6O_3$, [M-(NO_3)-(MeOH)]+), 415 (11.7%, [M-(NO_3)$_2$-(MeOH)]$^+$), 302 (72.6%, [(L+H)]$^+$).

[Cd(μ-L)Cl_2]$_2$·3DMF (**2**·3 DMF). **L** (0.065 g, 0.219 mmol) was added as a solid to a solution of $CdCl_2{\cdot}2.5H_2O$ (0.050 g, 0.219 mmol) in dmf (5 mL), and the mixture was stirred for 2 h at room temperature to give a colorless solution. The product was crystallized by gas phase diffusion of diethyl ether into the reaction mixture at room temperature, providing colorless crystals, which were dried under high vacuum. Yield (0.108 g 83% based on Cd), mp 163 °C (dec). IR (KBr): 3232, 3052, 2918, 2870, 1656, 1580, 1564, 1437, 1251, 751 cm^{-1}. ^{1}H NMR (DMSO-d_6, 200 MHz): δ 9.31 (bs, NH, 1H), 8.63-6.92 (m, 12H.), 5.72 (s, 2H). ^{13}C NMR (DMSO-d_6, 50 MHz) δ 163.6 (C=O of DMF), 162.0 (C^2 of imidazoline ring), 156.6 (C_5H_4N), 149.3 (C_5H_4N), 148.3 (C_5H_4N), 147.3 (C_5H_4N), 142.1 (C_5H_4N), 139.6 (C_5H_4N), 135.4 (C_5H_4N), 127.7 (C_5H_4N), 123.1 (C_5H_4N), 122.3 (C_5H_4N), 72.6 (C^4 of imidazoline ring), 66.5 (C^5 of imidazoline ring) 35.8 (CH_3 DMF), 30.8 (CH_3 DMF). MS (HR-FAB$^+$) *m/z*: 751.1345 (10%, -4.2 ppm for $C_{36}H_{30}N_{10}ClCd$, [M-$CdCl_2$-Cl]$^+$), 450 (100 %, [M-2Cl]$^{2+}$), 302 (32%, [L+H]$^+$).

X-ray crystallography

X-ray quality crystals were grown by vapor phase diffusion of diethyl ether into a concentrated solution of the complex in DMF. A summary of crystal data and refinement parameters for the structural analyses is given in Table 1. X-ray diffraction studies were performed on a Bruker-AXS diffractometer with a CCD area detector ($\lambda_{MoK\alpha}$=0.71073 Å, monochromator: graphite). Frames were collected at T = 293 K for complex **1** and T = 100 K for complex **2** via ω/Φ-rotation at 10 s per frame (SMART) [17]. The measured intensities were reduced to F^2 and corrected for absorption with SADABS (SAINT-NT) [18]. Corrections were made for Lorentz and polarization effects. Structure solution, refinement and data output were carried out with the SHELXTL-NT program package [19]. Non hydrogen atoms were refined anisotropically. C-H hydrogen atoms were placed in geometrically calculated positions using a riding model. N-H and O-H hydrogen atoms have been localized by difference Fourier maps, but their D-H distances and U_{iso} factors have been constrained. DMF solvent molecules are present in the crystal lattice of **2**·3DMF**,** of which two are disordered over two positions and one is disordered over three positions.

Conclusions

We have shown that *cis*-2,4,5-tri(2-pyridyl)imidazoline **L** forms monomeric and dimeric complexes with Cd(II) to give [Cd(L)(NO_3)$_2$(MeOH)] (**1**) and [Cd(μ-L)Cl_2]$_2$·3DMF (**2**·3DMF). In both cases the counteranions are bound to the metal atom, demonstrating that there is a competition between the nitrogen atoms and NO_3^-/Cl^- for the coordination sites of the metal. Since in the first case MeOH molecules were also included in the coordination sphere, the solvent may play an important role in the tuning of the structural topologies and nuclearity of these complexes.

Supplementary information

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, for **1**: CCDC No. 619404; for **2**: CCDC No. 619405. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Acknowledgements

This work was supported by Consejo del Sistema Nacional de Educación Tecnológica (COSNET) Grant No. 418.03-P. J.J.C.-G. thanks the support from Consejo Nacional de Ciencia y Tecnología (CONACYT) in the form of a scholarship. The authors are indebted to Dr. I. Rivero and Dr. D. Chávez of Instituto Tecnológico de Tijuana for analytical support, Instituto de Química-UNAM for a preliminary diffraction study of complex **2**, Dr. V. Jancik at IQ-UNAM, and Prof. P. J. Walsh at the University of Pennsylvania for their valuable contributions to this work.

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