



Journal of the Mexican Chemical Society

ISSN: 1870-249X

editor.jmcs@gmail.com

Sociedad Química de México

México

Campos Gaxiola, José J.; Höpfl, Herbert; Parra, Miguel
Mono and Dinuclear Cadmium(II) Complexes with the Ligand cis-2,4,5-tri(2-pyridyl)imidazoline
Journal of the Mexican Chemical Society, vol. 51, núm. 1, january-march, 2007, pp. 27-32
Sociedad Química de México
Distrito Federal, México

Available in: <http://www.redalyc.org/articulo.oa?id=47551106>

- How to cite
- Complete issue
- More information about this article
- Journal's homepage in redalyc.org

redalyc.org

Scientific Information System

Network of Scientific Journals from Latin America, the Caribbean, Spain and Portugal

Non-profit academic project, developed under the open access initiative

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

José J. Campos-Gaxiola,¹ Herbert Höpfl,² Miguel Parra-Hake^{1*}

¹ Centro de Graduados e Investigación, Instituto Tecnológico de Tijuana, Apartado Postal 1166, 22000 Tijuana, Baja California México. mparra@tectijuana.mx

² Centro de Investigaciones Químicas, Universidad Autónoma del Estado de Morelos, Av. Universidad 1001, Cuernavaca 62209, México. hhopf@ciq.uaem.mx

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, $[\text{Cd}(\text{L})(\text{NO}_3)_2(\text{MeOH})]$ (**1**) y $[\text{Cd}(\mu\text{-L})\text{Cl}_2]_2$ (**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 $\text{CH}\cdots\pi$. En la estructura del complejo **2** se observa sólo una interacción del tipo $\pi\text{-}\pi$ 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, $[\text{Cd}(\text{L})(\text{NO}_3)_2(\text{MeOH})]$ (**1**) and $[\text{Cd}(\mu\text{-L})\text{Cl}_2]_2$ (**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 $\text{CH}\cdots\pi$ interaction. In **2** only one intramolecular $\pi\text{-}\pi$ 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], $\pi\text{-}\pi$ [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 $(\text{cis-2,4,5-tri(2-pyridyl)imidazoline})_2\text{M}_2^{4+}$

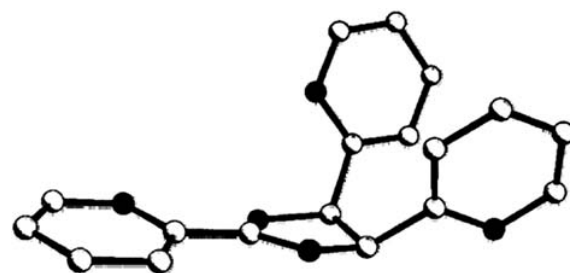
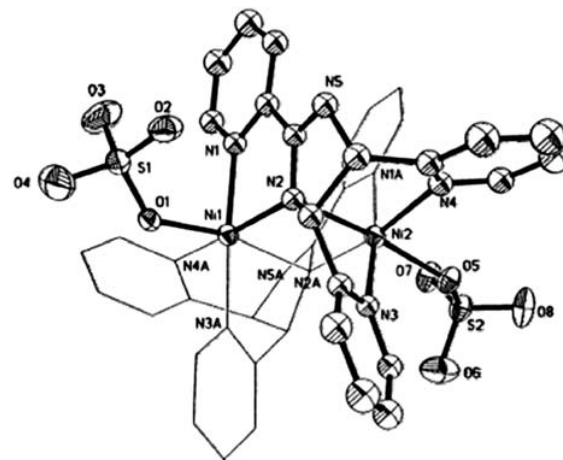


Fig. 1. Ball-and-stick drawing of the structure of **L**. The black spheres represent nitrogen atoms and the white spheres carbon atoms.



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.

Synthesis and General Characterization

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 NO₂⁻ stretching appear at 1435, 1383 and 1290



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.

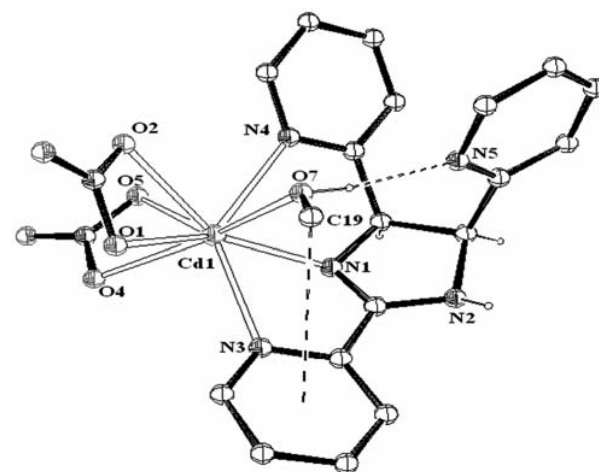


Fig. 3. Perspective view of the molecular structure of the monomeric complex $[\text{Cd}(\text{L})(\text{NO}_3)_2(\text{MeOH})]$ (**1**), showing the numbering scheme and the thermal ellipsoids at the 50% probability level (dashed lines indicate the H-bonding and a weak $\text{CH}\cdots\pi$ interaction).

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

	1	2 ·3DMF
empirical formula	C ₁₉ H ₁₉ CdN ₇ O ₇	C ₉₀ H ₁₀₂ Cd ₄ Cl ₈ N ₂₆ O ₆
<i>MW</i> (g mol ⁻¹)	569.81	2377.18
space group	<i>C</i> 2/ <i>c</i>	<i>P</i> -1
<i>a</i> , Å	28.914(2)	8.6335(6)
<i>b</i> , Å	9.6287(7)	12.8550(8)
<i>c</i> , Å	15.8354(12)	23.4957(15)
<i>α</i> , deg	90	76.872(10)
<i>β</i> , deg	97.772(10)	87.093(10)
<i>γ</i> , deg	90	81.5470(10)
<i>V</i> , Å ³	4368.1(6)	2511.5(3)
<i>Z</i>	8	1
ρ_{calc} (g cm ⁻³)	1.733	1.572
μ , mm ⁻¹	1.058	1.113
θ limits (°)	2 < θ < 25	2 < θ < 25
No. collected refl.	10187	11028
No. indep. refl. (<i>R</i> _{int})	3829 (2.14)	8132 (1.49)
No. observed refl. ^[a]	3415	7378
<i>R</i> _w ^b	0.0389	0.0377
<i>R</i> _w ^c	0.0414	0.0955
GOF	1.076	1.050
$\Delta\rho_{\text{max}}$ (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)
N(2)-H(2')...O(1)#1	0.85	2.17	2.980
O(7)-H(7')...N(5)#2	0.84	1.98	2.807
			∠ D-H...A (°)
			158
			171

^a Symmetry operators: #1 x, y, z #2 x, 1-y, -1/2 + z

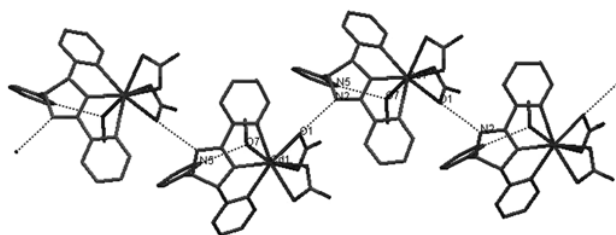
Table 3. Selected bond lengths (Å) and angles (°) for complex **2**·3DMF.

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

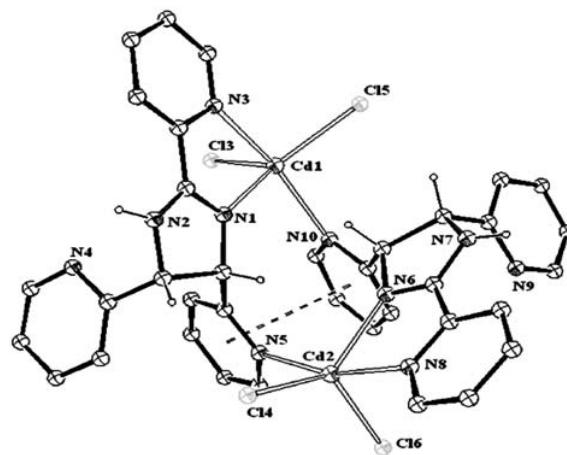
^a Symmetry operators: #1 -x+2,-y+1,-z+1 #2 -x+1,-y+2,-z+1.

fore shorter than those in $\{[\text{Cd}(\mu\text{-}3,3'\text{-pytz})(\text{NO}_3)_2(\text{MeOH})_2]\}_\infty$ [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 bipyra-

**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).

mid 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 $\tau = 0.49$ [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. 5.** Perspective view of the molecular structure of the dimeric complex $[\text{Cd}(\text{L})(\text{Cl})_2]_2$ (**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 $126.20(8)^\circ$ and $163.18(10)^\circ$, 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...centroid distance is 3.46 Å, thus being similar to those observed in related structures [16]. In the crystal lattice, intermolecular N-H...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 dms_o-d₆ 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)(NO₃)₂(MeOH)] (1). **L** (0.048 g, 0.162 mmol) was added as a solid to a solution of Cd(NO₃)₂·4H₂O (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. ¹H NMR (DMSO-d₆, 200 MHz): δ 9.52 (bs, NH, 1H), 8.60-6.80 (m, 12H), 5.81 (s, 2H). ¹³C NMR (DMSO-d₆, 50 MHz) δ 163.8 (C² of imidazoline ring), 156.5 (C₅H₄N), 149.3 (C₅H₄N), 148.5 (C₅H₄N), 147.7 (C₅H₄N), 142.1 (C₅H₄N), 140.1 (C₅H₄N), 135.9 (C₅H₄N), 128.3 (C₅H₄N), 123.6 (C₅H₄N), 122.5 (C₅H₄N), 122.0 (C₅H₄N), 72.2 (C⁴ of imidazoline ring), 66.7 (C⁵ of imidazoline ring). MS (HR-FAB⁺) m/z : 477.0197 (100%, -9.0 ppm for C₁₈H₁₅CdN₆O₃, [M-(NO₃)-(MeOH)]⁺), 415 (11.7%, [M-(NO₃)₂-(MeOH)]⁺), 302 (72.6%, [(L+H)]⁺).

[Cd(μ-L)Cl₂]₂·3DMF (2·3 DMF). **L** (0.065 g, 0.219 mmol) was added as a solid to a solution of CdCl₂·2.5H₂O (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. ¹H NMR (DMSO-d₆, 200 MHz): δ 9.31 (bs, NH, 1H), 8.63-6.92 (m, 12H), 5.72 (s, 2H). ¹³C NMR (DMSO-d₆, 50 MHz) δ 163.6 (C=O of DMF), 162.0 (C² of imidazoline ring), 156.6 (C₅H₄N), 149.3 (C₅H₄N), 148.3 (C₅H₄N), 147.3 (C₅H₄N), 142.1 (C₅H₄N), 139.6 (C₅H₄N), 135.4 (C₅H₄N), 127.7 (C₅H₄N), 123.1 (C₅H₄N), 122.3 (C₅H₄N), 72.6 (C⁴ of imidazoline ring), 66.5 (C⁵ of imidazoline ring) 35.8 (CH₃ DMF), 30.8 (CH₃ DMF). MS (HR-FAB⁺) m/z : 751.1345 (10%, -4.2 ppm for C₃₆H₃₀N₁₀ClCd, [M-CdCl₂-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 ($\lambda_{\text{MoK}\alpha} = 0.71073$ 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)(NO₃)₂(MeOH)] (**1**) and [Cd(μ-L)Cl₂]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 NO₃⁻/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.

References

1. Majumder, A.; Gramlich, V.; Rosair, G. M.; Batten, S.; Masuda, J. D.; Fallah, M.S.; Ribas, J.; Sutter, J. P.; Desplanches, C.; Mitra, S. *Cryst. Growth & Des.* **2006**, 6, 2355-2368.
2. Burchell, T. J.; Puddephatt, R. J. *Inorg. Chem.* **2005**, 44, 3718-3730.
3. Wang, R.; Jiang, F.; Zhou, Y.; Han, L.; Hong, M. *Inorg. Chim. Acta* **2005**, 358, 545-554.
4. Hosseini, M. W. *Acc. Chem. Res.* **2005**, 38, 313-323.
5. Balamaruan, V.; Jacob, W.; Mukherjee, J.; Mukherjee, R. *Cryst. Eng. Comm.* **2004**, 396-400.
6. Beatty, A. M. *Coord. Chem. Rev.* **2003**, 246, 131-143.
7. Biradha, K. *CrystEngComm* **2003**, 374-384.
8. Zou, R. Q.; Liu, C. S.; Huang, Z.; Hu, T. L.; Bu, X. H. *Cryst. Growth & Des.* **2006**, 6, 99-108.
9. Liu, C. B.; Yu, M. X.; Zheng, X. J.; Jin, L. P.; Gao, S.; Lu, S. Z. *Inorg. Chim. Acta* **2005**, 358, 2687-2696.
10. Roesky, H. W.; Andruh, M. *Coord. Chem. Rev.* **2003**, 236, 91-119.
11. Wang, X. L.; Qin, C.; Wang, E. B.; Xu, L. *Cryst. Growth & Des.* **2006**, 6, 2061-2065.
12. Hong, C. S.; Yoon, J. H.; Lim, J. H.; Ko, H. H. *Eur. J. Inorg. Chem.* **2005**, 4818-4821.
13. Chen, X. M.; Liu, G. F. *Chem. Eur. J.* **2002**, 8, 4811-4817.
14. Janiak, C. *J. Chem. Soc., Dalton Trans.* **2000**, 3885-3896.
15. Lehn, J.-M. *Supramolecular Chemistry: Concepts and Perspectives*; VCH Publishers: New York, 1995.
16. Desiraju, G. R. *Crystal Engineering: The Design of Organic Solids*; Elsevier: New York, 1989.
17. Séneque, O.; Giorgi, M.; Reinaud, O. *Chem. Commun.* **2001**, 984-985.
18. Itoh, M.; Nakazawa, J.; Maeda, K.; Mizutani, T.; Kodera, M. *Inorg. Chem.* **2005**, 44, 691-702.
19. Albrecht, M. *Chem. Rev.* **2001**, 101, 3457.
20. Leininger, S.; Olenyuk, B.; Stang, P. J. *Chem. Rev.* **2000**, 100, 853-908.
21. Larter, M. L.; Phillips, M.; Ortega, F.; Aguirre, G.; Somanathan, R.; Walsh, P. J. *Tetrahedron Lett.* **1998**, 39, 4785-4788.
22. Reedijk, J. In *Comprehensive Coordination Chemistry*; Wilkinson, G. Ed.; Pergamon Press: Oxford, 1987; Vol. 2, p. 73.
23. Parra-Hake, M.; Larter, M. L.; Ganzel, P.; Aguirre, G.; Ortega, F.; Walsh, P. J. *Inorg. Chem.* **2000**, 39, 5400-5403.
24. Cordes, D. B.; Bailey, A. S.; Caradoc-Davies, P. L.; Gregory, D. H.; Hanton, L. R.; Lee, K.; Spicer, M. D. *Inorg. Chem.* **2005**, 44, 2544-2552.
25. Du, M.; Bu, X. H.; Huang, Z.; Chen, S. T.; Guo, Y. M. *Inorg. Chem.* **2003**, 42, 552-559.
26. Bu, X. H.; Liu, H.; Du, M.; Wong, K. M.; Yam, V. W. *Inorg. Chim. Acta* **2002**, 333, 32-40.
27. Pretsch, E.; Bühlmann, P.; Affolter, C. *Structure Determination of Organic Compounds*; Springer: Berlin, 2000, p. 167.
28. Lipard, S. J. *Prog. Inorg. Chem.* **1968**, 8, 109-193.
29. Burchell, T. J.; Puddephatt, J. R. *Inorg. Chem.* **2006**, 45, 650-659.
30. Yang, X.; Randford, J. D.; Vittal, J. J. *Cryst. Growth Des.* **2004**, 4, 781-788.
31. Aakeröy, C. B.; Beatty, A. M.; Desper, J.; O'Shea, M.; Valdés-Martínez, J. *Dalton Trans.* **2003**, 3956-3962.
32. Withersby, M. A.; Blake, A. J.; Champness, N. R.; Cooke, P. A.; Hubberstey, P.; Li, W. S.; Schröder, M. *Inorg. Chem.* **1999**, 38, 2259-2266.
33. Chopra, D.; Guru Row, T. N. *Cryst. Growth Des.* **2006**, 6, 1267-1270.
34. Go, Y.; Wang, X.; Anokhina, E. V.; Jacobson, A. J. *Inorg. Chem.* **2004**, 43, 5360-5367.
35. Frontera, A.; Garau, C.; Quiñero, D.; Ballester, P.; Costa, A.; Deyva, P. M. *Org. Lett.* **2003**, 5, 1135-1138.
36. Addison, A. W.; Rao, N. T.; Reedijk, J.; Rijn, J.; Verschoor, G. J. *Chem. Soc. Dalton Trans.* **1984**, 1349-1356.
37. Liu, C. S.; Shi, X. S.; Li, J. R.; Wang, J. J.; Bu, X. H. *Cryst. Growth Des.* **2006**, 6, 656-663.
38. Liu, C. S.; Chen, P. Q.; Yang, E. C.; Tian, J. L.; Bu, X. H.; Li, Z. M.; Sun, H. W.; Lin, Z. *Inorg. Chem.* **2006**, 45, 5812-5821.
39. Bruker Analytical X-ray System. SMART: Bruker Molecular Analysis Research Tool, Version 5.618, **2000**.
40. Bruker Analytical X-ray System. SAINT + NT, Version 6.04, **2001**.
41. Sheldrick, G. M. SHELX86, Program for Crystal Structure Solution, University of Göttingen, Göttingen (Germany), **1986**.
42. Bruker Analytical X-ray System. SHELXTL-NT Version 6.10, **2000**.