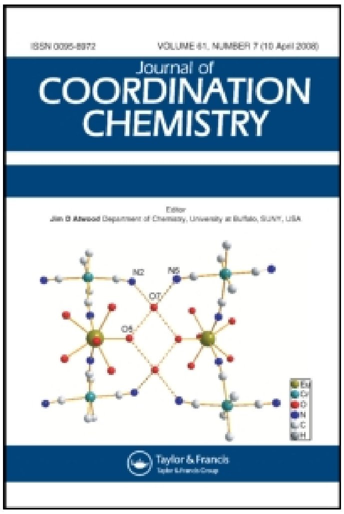

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis and crystal structure of a macrocyclic complex precursor: Bis-(2-amino-1-methyliminobenzene)1,2-ethane nickel(II) dichloride

J. R. Anacona[a]; Roxibel Durán[a]; Blanca Najera[b]; Cecilia Rodriguez-Barbarín[b]
[a] Departamento de Quimica, Universidad de Oriente, Cumaná, Venezuela [b] Facultad de Ciencias Quimicas, Universidad Autónoma de Nuevo León, Monterrey, Mexico

To cite this Article Anacona, J. R. , Durán, Roxibel , Najera, Blanca and Rodriguez-Barbarín, Cecilia(2005) 'Synthesis and crystal structure of a macrocyclic complex precursor: Bis-(2-amino-1-methyliminobenzene)1,2-ethane nickel(II) dichloride', Journal of Coordination Chemistry, 58: 16, 1395 — 1400

To link to this Article: DOI: 10.1080/00958970500048729

URL: http://dx.doi.org/10.1080/00958970500048729

Journal of Coordination Chemistry
Vol. 58, No. 16, 10 November 2005, 1395–1400

Synthesis and crystal structure of a macrocyclic complex precursor: Bis-(2-amino-1-methyliminobenzene)1,2-ethane nickel(II) dichloride

J.R. ANACONA†*, ROXIBEL DURÁN†, BLANCA NAJERA‡
and CECILIA RODRIGUEZ-BARBARÍN‡

†Departamento de Quimica, Universidad de Oriente, Apartado Postal 208, Cumaná, Venezuela
‡Facultad de Ciencias Quimicas, Universidad Autónoma de Nuevo León, Monterrey, Mexico

(Received 29 December 2003; in final form 23 December 2004)

NiLCl_2 (L = bis-(2-amino-1-methyliminobenzene)1,2-ethane) crystallizes in space group P-1 with $a = 9.042(2)$, $b = 10.263(10)$, $c = 11.045(2)$ Å, $\alpha = 94.76(10)$, $\beta = 108.30(10)$, $\gamma = 109.86(10)^\circ$, $Z = 2$, and represents a precursor of a tetradentate azamacrocyclic complex. The structure is stabilized by a system of intramolecular and intermolecular H-bonding involving chloride ions and nitrogen atoms. The coordination geometry about nickel(II) is slightly distorted octahedral.

Keywords: Nickel; Azamacrocycle; Hydrogen bonding; Structure

1. Introduction

Transition metal complexes containing macrocycles have been of considerable interest in terms of structural chemistry and biological function [1]. This field has undergone spectacular growth during the past years and extensive work has been carried out in many areas [2–10]. This growth has largely been due to the synthesis of multidentate ligands and the complexes such ligands form with metal ions.

Recognition of the importance of complexes containing macrocyclic ligands led to considerable effort directed towards the development of reliable syntheses of these interesting and important compounds. For many years the results were largely unsuccessful because of low yields, many side products and large volumes of solvents that were required to give sufficient dilution to minimize polymerization and favor cyclization.

The function of the metal ion in *in situ* syntheses of this type has been the source of much discussion, and when the directive influence of the metal ion controls the steric

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*Corresponding author. E-mail: juamacona@hotmail.com

Journal of Coordination Chemistry
ISSN 0095-8972 print: ISSN 1029-0389 online
DOI: 10.1080/00958970500048729

course of a sequence of stepwise reactions, the kinetic template effect is considered to be operative. As an example of this and continuing with previous studies [11–15], we report here the isolation, characterization and crystal structure of a macrocyclic complex precursor containing the bis-(2-amino-1-methyliminobenzene)1,2-ethane ligand.

2. Experimental

2.1. *Physical measurements*

Conductance measurements were made using a Wayne Kerr Universal Bridge. The conductivity cell was calibrated with aqueous KCl. The IR spectra of the ligand and its metal complexes in KBr pellets were recorded in the 4000–400 cm^{-1} range with a Perkin-Elmer Series 2000 spectrophotometer. FTIR spectra as polyethylene pellets were recorded between 450–120 cm^{-1} using a Brucker IFS 66V spectrophotometer. UV–vis. spectra were recorded using a Perkin-Elmer recording spectrometer. C, H, and N were analyzed on a LECO CHNS 932 model microanalytical instrument. The metal content of the complex was determined with a Perkin-Elmer atomic absorption spectrophotometer in solutions prepared by decomposition of the complex in conc. HCl and conc. HNO_3 (3 : 1) followed by dilution in water. Magnetic susceptibility was measured on a Johnson Matthey Susceptibility Balance at room temperature using mercury(II) tetrathiocyanato-cobaltate(II) as calibrant.

2.2. *Materials*

Published methods were used to prepare L by $LiAlH_4$ reduction of the precursor di-imine [16]. Solvents were distilled over appropriate drying agents prior to use. All other chemicals were commercial materials of analytical grade. Unless otherwise stated the reactions were carried out under dry N_2.

2.3. *Preparation of NiLCl$_2$*

The ligand L (1 mmol) and $NiCl_2$ (1 mmol) were mixed in dry methanol (50 mL). The mixture was refluxed for two days and the boiling solution was concentrated to 5 mL. This solution was left standing at low temperature (5°C) and in a few weeks, blue prismatic crystals were obtained. Yield 72%. Anal. Calcd. for $[C_{16}H_{22}Cl_2N_4Ni]\%$: C, 48.04; H, 5.68; N, 14.00; Ni, 14.67. Found: C, 48.36; H, 5.88; N, 13.82; Ni, 14.71.

2.4. *X-ray crystallography*

For X-ray structural determination a single crystal with approximate dimensions $0.50 \times 0.34 \times 0.12$ mm was selected. The intensities of 6105 reflections were measured with a Siemens P4 diffractometer (graphite monochromated Mo-Kα radiation, $\lambda = 0.71073$ Å, by the ω scan technique, 2θ range 2.98–60.0°. The structure was solved by direct methods and refined by full-matrix least-squares techniques, with anisotropic approximation for all non-hydrogen atoms by the SHELXL-97 program [17–19]. Hydrogen atoms were included, some from difference Fourier maps and the rest in calculated positions, and refined in the riding mode with isotropic factor related to the bonded atoms. Analytical absorption correction [μ (MoKα) = 1.387 mm^{-1}] was applied by the face-indexed integration method ($T_{\min} = 0.560$ and $T_{\max} = 0.687$).

3. Results and discussion

Elemental analyses agree well with the stoichiometry of the nickel(II) complex. It is colored and appears to be air-stable and soluble in methanol. The experimental conductivity value in methanol falls in the 1 : 1 electrolyte range suggesting that one chloride anion is coordinated to the metal.

The complex has a magnetic moment of 2.75 BM at room temperature and lies in the range associated with d^8 systems with two unpaired electrons suggesting high spin octahedral nickel(II). The IR spectrum reveals the absorptions expected for the structure. Phenyl ν_{CH} vibrations at 3000–3100 cm^{-1} and aliphatic ν_{CH} stretchings at 2900–3000 cm^{-1}. A strong band at 465 cm^{-1}, attributable to M-N stretching vibrations, and the characteristic bands for the NH$_2$ moiety in the 3260–3200 cm^{-1} range can also be assigned. These latter are displaced relative to the free ligand suggesting coordination.

The u.v. visible spectrum of the complex in methanol solution presents one absorption maxima at 322 nm, presumably due to intraligand excitation.

The observed triplet–triplet absorptions and the assignments for the complex considering octahedral geometry are: 760 nm ($^3A_{2g} \rightarrow {}^3T_{2g}$, ν_1), 570 nm ($^3A_{2g} \rightarrow {}^3T_{2g}$ (F), ν_2) and 455 nm which may have charge transfer character.

An ORTEP representation, including the atomic numbering scheme is given in figure 1. The molecular interactions in the crystal extended along the a axis as shown in figures 2 and 3. The relevant crystal data and structure parameters are summarized

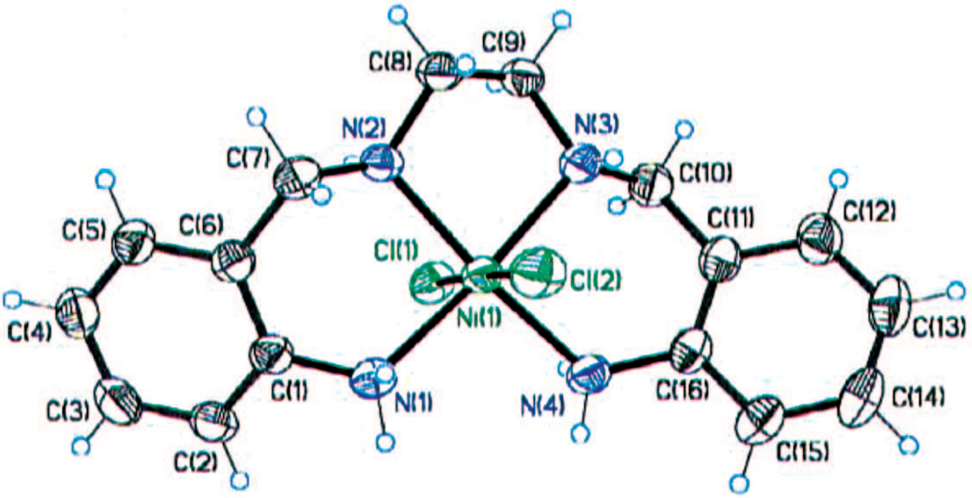

Figure 1. A molecular representation of NiLCl$_2$ with the atomic labelling scheme shown. Thermal ellipsoids are at the 30% probability level.

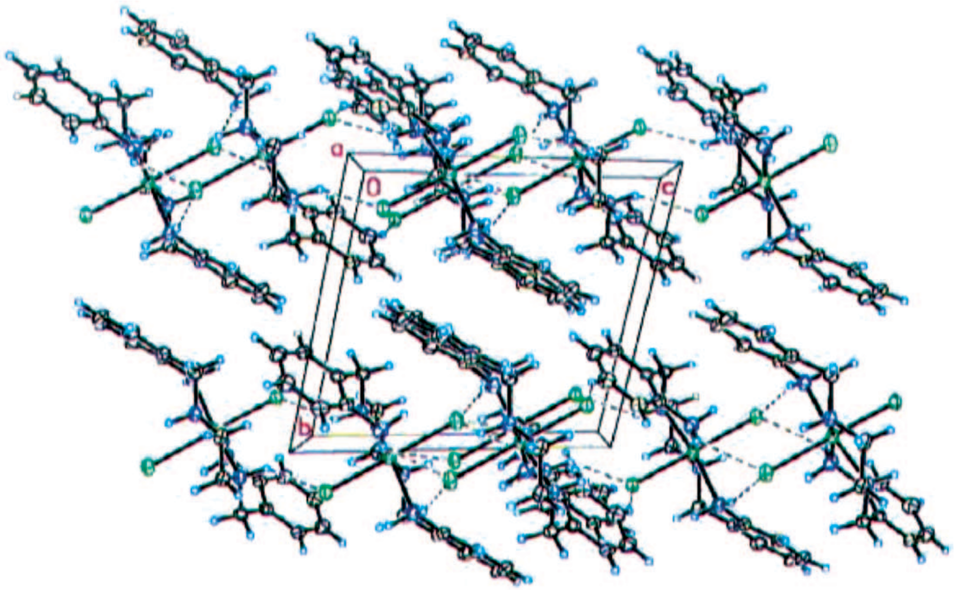

Figure 2. Crystal packing of the $NiLCl_2$ complex, view perpendicular to the *a* axis, showing extended intermolecular H-bonding.

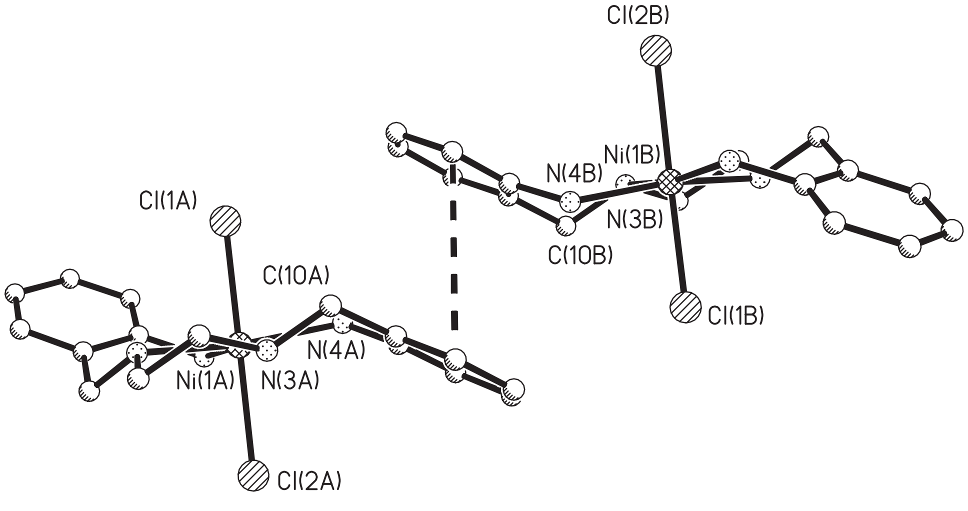

Figure 3. The displaced stacking complex molecules are arranged within the crystal forming a weak pi…pi interaction [4.148 Å] between benzene rings of symmetry related molecules.

in table 1 while table 2 gives selected bond lengths and bond angles with estimated standard deviations. The coordination geometry about nickel(II) in the complex is slightly distorted octahedral (root mean square deviation 0.144 Å for N1, N2, N3, N4 coordination plane). Nickel ion is bonded to the four amino nitrogens of L and to two chlorides occupying the apical positions of the octahedral coordination

Table 1. Crystallographic data.

Empirical formula	$C_{16}H_{22}Cl_2N_4Ni$
Color, habit	Blue, prismatic
Crystal size	$0.50 \times 0.34 \times 0.12$ mm
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	$a = 9.042(2)$ $b = 10.2630(10)$ $c = 11.045(2)$ Å $\alpha = 94.760(10)$ $\beta = 108.300(10)$ $\gamma = 109.860(10)^\circ$
Volume	894.4(3) Å^3
Z	2
Formula weight	399.99
Density (calculated)	1.485 g cm^{-3}
2θ range	2.98 – 60.00°
Absorption coefficient	1.387 mm^{-1}
Reflections collected	6105
Independent reflections	5192 ($R_{\text{int}} = 0.0137$)
$< I / \sigma(I) >$ (all data)	16.51
Final R indices ($I > 2\sigma(I)$)	$R_1 = 0.0314$, $wR_2 = 0.0777$
Final R indices (all data)	$R_1 = 0.0439$, $wR_2 = 0.0840$

Table 2. Selected bond distances (Å) and bond angles (°) for the $NiLCl_2$ complex.

Bond distances			
Ni(1)–N(3)	2.0773(14)	Ni(1)–N(1)	2.1113(15)
Ni(1)–N(4)	2.1355(15)	Ni(1)–N(2)	2.0685(14)
Ni(1)–Cl(1)	2.4380(6)	Ni(1)–Cl(2)	2.5568(6)
Bond angles			
N(3)–Ni(1)–N(1)	169.16(65)	N(3)–Ni(1)–N(4)	89.87(6)
N(1)–Ni(1)–N(4)	97.40(6)	N(4)–Ni(1)–N(2)	170.00(5)
N(1)–Ni(1)–N(2)	89.88(6)	N(2)–Ni(1)–Cl(2)	92.35(4)
N(3)–Ni(1)–Cl(1)	95.54(4)	N(1)–Ni(1)–Cl(1)	93.17(5)
N(4)–Ni(1)–Cl(1)	84.42(4)	N(2)–Ni(1)–Cl(1)	88.35(4)
N(3)–Ni(1)–Cl(2)	86.97(4)	N(1)–Ni(1)–Cl(2)	84.39(5)
N(4)–Ni(1)–Cl(2)	95.17(4)	Cl(1)–Ni(1)–Cl(2)	177.46(17)

geometry. The two phenyl rings are planar (root mean square deviations 0.005 and 0.004 Å and are mutually inclined making an angle of 37.3° between normals to their mean planes.

The molecular structure shows intramolecular interactions between coordinated chlorides and amine groups [N1-H1A.....Cl2 2.528, N2-H2A.....Cl1 2.666, N3-H3A.....Cl2 2.677 Å, between H.....Cl distances and N1...Cl2 3.153(2), N2...Cl1 3.152(2), N3...Cl2 3.081(2) Å] with distances shorter than van der Waals distances between N...Cl of 3.30 Å. The crystal structure shows, in addition, intermolecular H-bonding between Cl ions of one molecule and hydrogens of amine nitrogen atoms of symmetry related molecules at both sides of a complex molecule, as can be appreciated in figure 2. Table 3 gives intra and intermolecular hydrogen bond information. These intermolecular interactions form parallel planes of molecules in an approximately diagonal orientation within the unit cell. The complex molecules in the crystal form weak pi...pi interactions [4.148 Å] between benzene rings of symmetry-related molecules in a displaced stacking arrangement, as can be appreciated in figure 3.

Table 3. Hydrogen bonds with H. . . .A < r(Å) + 2.000 Å and D-H. . . .A > 110°. D represents the donor atom and A the acceptor atom.

D	H	A	Symmetry for A	D-H	H. . . .A	D. . . .A	D-H. . . .A
N(1)	H(1A)	Cl(2)	x, y, z	0.94	2.53	3.153(2)	124
N(1)	H(1B)	Cl(2)	$-x+2, -y+2, -z+1$	0.92	2.71	3.392(2)	132
N(2)	H(2A)	Cl(1)	$-x+1, -y+2, -$z	0.94	2.58	3.275(1)	131
N(2)	H(2B)	Cl(1)	x, y, z	0.94	2.67	3.152(2)	113
N(3)	H(3A)	Cl(2)	x, y, z	0.93	2.68	3.208(2)	117
N(4)	H(4A)	Cl(2)	$-x+2, -y+2, -z+1$	0.90	2.64	3.506(2)	162
N(4)	H(4B)	Cl(1)	x, y, z	0.93	2.45	3.081(2)	125

Supplementary data

Full lists of crystallographic data are available from the authors upon request.

Acknowledgments

J.R. Anacona and R. Durán thank the Universidad de Oriente for financial support.

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