Synthesis and Characterization of Cu(II) and Mono- and Dinuclear Pb(II) Complexes Derived from 3,5-Diacetyl-1,2,4-triazole

P. Souza\(^*\), A. I. Matesanz\(^a\), A. Arquerob, V. Fernandez\(^a\)

\(^a\) Departamento de Química (C–VIII), Facultad de Ciencias,
Universidad Autónoma de Madrid, Cantoblanco, E-28049-Madrid, Spain

\(^b\) Departamento A.T.S.I., Facultad de Informática, Universidad Politécnica de Madrid,
Montegancedo s/n, E-28660-Boadilla del Monte, Madrid, Spain

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Triazole Hydrazones. Copper(II), Lead(II). Macro Ligand

Template 1:1 condensation of 3,5-diacetyl-1,2,4-triazole with thiocarbohydrazide or carbohydrazide in the presence of 1 equivalent of Pb(SCN)\(_2\) produces mononuclear [2+1] complexes 1 and 3. The analogous reaction with thiosemicarbazide and semicarbazide produces the dinuclear [1+2] complex 2 and the mononuclear metal free 4. The carbohydrazide derivative 3 reacts with the carbohydrazide or the 1,3-diaminopropane to yield the macrocyclic dinuclear complexes 5 and 6.

Direct reaction of 3,5-diacetyl-1,2,4-triazole with thiocarbohydrazide, carbohydrazide, thiosemicarbazide and semicarbazide leads to open [1+1] ligands L\(_1\), L\(_2\), L\(_3\), L\(_4\), and closed [1+1] ligands (mesocyclic ligands) L\(_5\) and L\(_6\) were prepared by addition of 1 equivalent of LiOH to the reaction mixture.

The reaction of open and mesocyclic [1+1] ligands with copper(II) salts gives [CuLX\(_2\)] and [Cu\(_2^+L_2\)] complexes. All these compounds have been characterized by \(^1\)H NMR, IR, electronic and mass spectra and by analytical data.

Introduction

Polyazamacrocycles constitute a huge collection of efficient complexing agents for a large number of transition metal cations [1, 2].

A synthetic methodology based upon the metal-directed condensation of heterocyclic dialdehydes or diketones with linear diamines to form macrocyclic polyimines has been applied for the synthesis of a wide range of imine macrocyclic complexes and provides a well established synthetic procedure for the preparation of these compounds [3]. Heterocycles have often been used as building subunits for macrocyclic systems [4].

1,2,4-Triazole derivatives are a class of azole compounds that can bind as either 2,4- or 1,2-bridging nitrogen-donor ligands [5–7]. The 1,2-bridging mode is known to yield polynuclear coordination compounds [5–7]. The mechanism of exchange interactions between paramagnetic centres bridged by azolate ligands (triazolate, imidazolate) has been actively investigated in the last few years [8–10]. The triazole heterocycle was selected not only for its symmetry, but also because the increased acidity of the N–H as a proton-ionizable centre [11] which facilitates the metal coordination. The capability of the triazole to generate a negative charge is the most important difference between this system and the related well known diacylpyridine based macrocycles [12].

We have been using 3,5-diacetyl-1,2,4-triazole as building block of macrocyclic Schiff bases in condensation reactions with thio- and semicarbazide, thio- and carbohydrazide.

In this paper we describe the synthesis and characterization of macrocyclic systems by templated [2+2] condensations and the isolation of various [1+1] open and cyclic ligands and their complexes.

Results and Discussion

We previously considered the synthesis of the ligands by the condensation of 3,5-diacetyl-1,2,4-triazole with thiocarboxyhydrazide (L\(_1\)), carbohydrazide (L\(_2\)), thiosemicarbazide (L\(_3\)) and semicarbazide (L\(_4\)). The same condensation reaction for
thiocarbohydrazide and carbohydrazide in presence of LiOH yields the new mesocyclic [1+1] (L^5) and (L^6) ligands.

Curtis [13] and others reported the first of a number of pioneering template reactions for macrocyclic systems and demonstrated the selective formation of [2+2] macrocycles by use of large metal ions such as lead(II), barium(II), silver(I) or lanthanides as templates [12].

We then tried to use the size of the lead ion to control the formation of [2+2] products [14]. However, these previous studies yielded [2+1] products with Pb(II) complexed (1, 2, 3) in all of them except for the product of the condensation reaction of 3,5-diacetyl-1,2,4-triazole and semicarbazide which was an organic molecule [2+1] (4) (Scheme 1).

The desired [2+2] systems (5 and 6) were prepared by stirring product 3 with carbohydrazide or propyldiamine. The IR spectra of these solids showed no absorptions which could be assigned to unreacted carbonyl groups, but exhibited absorptions centered at 1619, 1655 and 2059 cm^{-1} assigned to imine and enyl groups, indicative of deprotonation in the macrocyclic ring [15].

Initial attempts to prepare L^7 and L^8 by the reaction of 2 equivalents of 3,5-diacetyl-1,2,4-triazole with 2 equivalents of carbohydrazide were unsuccessful and the IR spectrum of the resulting white solid suggested that it was a single compound. The presence of a strong and broad absorption at 1694 and of a medium absorption at 1625 cm^{-1} were strongly indicative of the presence of monocondensated 3,5-diacetyl-1,2,4-triazole. The microanalysis is compatible with open chain L^7 [16].

The analogous L^1 was obtained in good yield by the same method involving the reaction of 3,5-diacetyl-1,2,4-triazole with thiocarbazide.

The reaction of 3,5-diacetyl-1,2,4-triazole with thiosemicarbazide or semicarbazide in 1:1 ratio afforded the open chain ligands L^3 and L^4. The EI mass spectrum of the L^4 exhibited an intense peak at \( m/z \) 210 [M^+] and daughter ions of this species (Scheme 2). On the other hand the EI mass spectrum of L^3 (Fig. 1) showed molecular ions at \( m/z \) 226 and \( m/z \) 299 of greatly reduced abundance (<10%) [17] which consisted of a mixture of L^3 (1:1) and the 1:2 derivative, that does not modify the L^3 microanalysis.

Due to the low solubility in common solvents, only the \(^1\)H NMR in CD_3SOCD_3 of L^3 and L^5 have been recorded.

The sharp singlet signal at 15.0 ppm in the \(^1\)H NMR spectrum of L^3 has been assigned to the ionizable proton which has a strong interaction with the carbonyl group of the molecule [11].

The \(^1\)H NMR spectrum of L^5 differs slightly from that of L^3, and clearly demonstrates the absence of an interaction of the ionizable proton, \( \delta \) 12.5 ppm. Two sharp singlets at \( \delta \) 11.0 ppm and 10.3 ppm are assigned to NH groups.

All of the experiments described above suggest that the products of the condensation of 3,5-diacetyl-1,2,4-triazole with carbazides are [1+1]
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\text{L}^1, \text{L}^2
\]

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\text{L}^3, \text{L}^4
\]

\[
\text{L}^5, \text{L}^6
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\[
\text{L}^7, \text{L}^8
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\[\text{H}_3\text{C} - \text{N} - \text{N} - \text{CH}_3 + \text{H}_2\text{NNHCNHNH}_2 \xrightarrow{\text{EtOH/H}_2\text{O}} 2\text{h. reflux} \rightarrow \text{L}^1\]

\[\text{H}_3\text{C} - \text{N} - \text{N} - \text{CH}_3 + \text{H}_2\text{NNHCONNH}_2 \xrightarrow{\text{EtOH/H}_2\text{O}} 2\text{h. reflux} \rightarrow \text{L}^2\]

\[\text{H}_3\text{C} - \text{N} - \text{N} - \text{CH}_3 + \text{H}_2\text{NNHCNHNH}_2 \xrightarrow{\text{EtOH/H}_2\text{O}} 2\text{h. reflux} \rightarrow \text{L}^3\]

\[\text{H}_3\text{C} - \text{N} - \text{N} - \text{CH}_3 + \text{H}_2\text{NNHCONNH}_2 \xrightarrow{\text{EtOH/H}_2\text{O}} 2\text{h. reflux} \rightarrow \text{L}^4\]

\[\text{H}_3\text{C} - \text{N} - \text{N} - \text{CH}_3 + 1) \text{LiOH} \xrightarrow{\text{EtOH/H}_2\text{O}} 2) \text{H}_2\text{NNHCNHNH}_2 \xrightarrow{\text{EtOH/H}_2\text{O}} 2\text{h. reflux} \rightarrow \text{L}^5\]

\[\text{H}_3\text{C} - \text{N} - \text{N} - \text{CH}_3 + 1) \text{LiOH} \xrightarrow{\text{EtOH/H}_2\text{O}} 2) \text{H}_2\text{NNHCONNH}_2 \xrightarrow{\text{EtOH/H}_2\text{O}} 2\text{h. reflux} \rightarrow \text{L}^6\]
open chain (L₁, L₂, L₃, L₄) and [1+1] mesocyclic (L₅, L₆) species.

We have studied the reactivity of the [1+1] open chain ligands (L₁, L₂, L₃, L₄) with copper(II) chloride and of the [1+1] mesocyclic ligands (L₅, L₆) with copper(II) perchlorate. The microanalytical data of the complexes correspond to [Cu(LH₂)X₂], where LH₂ = L₁, L₂, L₃, L₄, L₅, and to [CuL], where L = dianion of LH₂ [18].

The IR spectra in the 1700–700 cm⁻¹ range of the ligands are extremely rich, as are the spectra of their complexes. Coordination via the azomethine nitrogen and loss of hydrogen in 12 yield bands in the 1580–1660 cm⁻¹ region. Coordination by the thione group changes the position and intensity of the bands attributable to the thioamide group.

The spectrum of complex 11 shows fundamental vibrational modes of the perchlorate anion ν₃ (1109 cm⁻¹) and ν₄ (627 cm⁻¹) (Tₐ symmetry) [19] and does not contain any band assignable to the vibrations ν₁ and ν₂, forbidden in Tₐ symmetry, confirming that the perchlorate anions are not coordinated.

The lack of any signals assignable to the characteristic modes of the perchlorate anion in the IR spectrum of 12 and the microanalytical data confirm the loss of perchlorate anions and deprotonation of the heterocycle.

Absorption spectra for the series were obtained in the UV/VIS region over the range 200–800 nm.

All absorptions higher in energy than 435 nm (23000 cm⁻¹) correspond to intraligand electronic transitions. A comparison of the spectra of free and coordinated ligands shows a persistent intraligand band at ca. 300 nm. A common ligand to metal charge transfer occurs between 360 and 330 nm for each Cu(II) complex, and is assigned as a S → Cu(II) transition [20].

The shifts in charge transfer energies are consistent with a greater polarization of the sulfur atoms brought about by a structural rearrangement of the ligand [21].

**Experimental**

L-Lactic acid, hydrazine hydrate, carbohydrazide, thioecarbohydrazide, semicarbazide hydrochloride, thiosemicarbazide, copper(II) chloride dihydrate, copper(II) perchlorate hexahydrate, lithium hydroxide monohydrate and lead(II) thiocyanate were commercial products of highest
chemical grade. Solvents were purified according to standard procedures.

IR spectra in the 4000–400 cm⁻¹ range were recorded from KBr pellets on a Bomen spectrophotometer. UV/VIS spectra in dimethylformamide solution were run in a Pye-Unicam Sp-8-100 spectrophotometer. ¹H NMR spectra were recorded on a Bruker WH-200 spectrometer system in CD₃SOCD₃ with TMS as the internal standard. El mass spectra were recorded on a VG Auto Spec. Solutions were used to determine Pb by atomic absorption spectroscopy in a Hitachi Z-8200 spectrophotometer with Zeeman corrector. Elemental C, H, N analyses were carried out by the Servicio Interdepartamental de Investigación (SIDI) of our University.

General procedure for the preparation of L¹–L⁴ ligands

To 1.6 mmol of the diamine dissolved in 20 ml of ethanol-water mixture (1:1) heated to 60 °C, 1.6 mmol of 3,5-diacetyl-1,2,4-triazole dissolved in ethanol were added. The mixture was stirred at 60 °C for 2 h. The separated solid was collected by filtration, washed with ethanol, and recrystallized from ethanol.

Triazolthiocarbazone (L¹): yellow solid; yield 73%; m.p. 135 °C; IR (KBr) 3394, 3382 (N-H), 1701 (C=O), 1616 (C=N), 799 (C=S) cm⁻¹. 

Elemental analyses of C₇H₁₈N₇O₅S (243) 
Calcd C 34.85 H 4.56 N 40.60%, 
Found C 34.34 H 4.74 N 39.97%.

Triazolcarbazone monohydrate (L²): white solid; yield 95%; m.p. 260 °C; IR (KBr) 3413 (OH), 3326 (N-H), 1694 (C=O), 1625 (C=N) cm⁻¹.

Elemental analyses of C₇H₁₃N₇O₅ (243) 
Calcd C 34.57 H 5.35 N 40.33%, 
Found C 34.55 H 5.38 N 40.16%.

Triazolthiosemicarbazone dihydrate (L³): yellow solid; yield 26%; m.p. 184 °C; ¹H NMR (DMSO-d₆) δ 14.98 (s, 1H, NH triazol), 11.0 (s, 1H, NH amine), 8.41 (s, 2H, NH₂), 2.37, 2.32 (s, 3H, CH₃); IR (KBr) 3386 (OH), 3267 (NH₂), 1699 (C=O), 1618 (C=N), 847 (C=S) cm⁻¹; mass spectrum m/e 226 (M⁺).

Elemental analyses of C₇H₁₈N₈O₅S₂ (262) 
Calcd C 32.10 H 5.30 N 32.10%, 
Found C 32.19 H 5.41 N 31.94%.

Triazolsemicarbazone dihydrochloride trihydrate (L⁴): white solid; yield 15% m.p. 240 °C; IR (KBr) 3425 (OH), 3315 (NH₂), 1680, 1665 (C=O), 1587 (C=N) cm⁻¹; mass spectrum m/e 210 (M⁺).

Elemental analyses of C₇H₁₈N₈O₅C₁₂ (337) 
Calcd C 25.00 H 5.40 N 25.00%, 
Found C 25.03 H 5.49 N 24.93%.

General procedure for the preparation of L⁵ and L⁶ ligands

To 1.6 mmol of carbohydrazide or thiocarbohydrazide dissolved in 20 ml of ethanol-water mixture (1:1) heated to 60 °C, 1.6 mmol of 3,5-diacetyl-1,2,4-triazole and 1.6 mmol of LiOH dissolved in ethanol were added. The mixture was stirred at 60 °C for 2 h. The solid which separated was collected by filtration, washed with ethanol, and dried in vacuo.

(2,8-Dimethyl-5-thione-3,4,6,7,10,11,12-heptaazabicyclo[7.2.1]dodeca-2,7,11,12-tetraene)penta-hydrate (L⁵): yellow solid; yield 24%; m.p. >260 °C; ¹H NMR (DMSO-d₆) δ 12.52 (s, 1H, NH triazole), 10.95, 10.12 (s, 1H, NH amine), 2.49, 2.48 (s, 3H, CH₃); IR (KBr) 3349 (OH), 3197 (NH), 1612 (C=O), 796 (C=S) cm⁻¹.

Elemental analyses of C₇H₁₉N₇O₅S (313) 
Calcd C 26.84 H 6.07 N 31.34%, 
Found C 26.71 H 5.97 N 31.49%.

(2,8-Dimethyl-5-Oxo-3,4,6,7,10,11,12-heptaazabicyclo[7.2.1]dodeca-2,7,11,12-tetraene)tetr-hydrate (L⁶): cream solid; yield 43%; m.p. >260 °C; IR (KBr) 3425 (OH), 3219 (NH), 1677 (C=O), 1626 (C=N) cm⁻¹.

Elemental analyses of C₇H₁₇N₇O₅ (279) 
Calcd C 30.11 H 6.09 N 35.12%, 
Found C 30.40 H 5.97 N 35.45%.

General procedure for the preparation of 1–4

To a suspension of Pb(SCN)₂ (1.3 mmol) in EtOH at 60 °C a solution of 3,5-diacetyl-1,2,4-triazole (1.3 mmol) in EtOH/H₂O (1:1) the yellow products precipitated and were filtered off.

Bistriazolthiocarbazone lead dithiocyanate monohydrate (1): orange solid; yield 50%; m.p. 90 (d) °C; IR (KBr) 3426 (OH), 2053 (NCS), 1726 (C=O), 1617 (C=N), 786 (C=S) cm⁻¹.

Elemental analyses of C₁₃H₁₈N₁₂O₂S₃Pb 
Calcd C 24.56 H 3.10 N 23.86 Pb 29.89%, 
Found C 24.80 H 2.95 N 23.60 Pb 28.93%.

Triazolbis(thiosemicarbazone) bis(lead dithiocyanate) trihydrate (2): yellow solid; yield 19%:
m.p. 140 (d) °C; IR (KBr) 3401 (OH), 3323 (NH₂), 2071, 2047 (NCS), 1604 (C =O), 1700 (C =O), 1685 (C =N), 1655 (C =O), 1655 (C =O), 1185 (C –O ) cm⁻¹. UV/VIS: 305, 340, 790 nm.

These complexes (7–10) were also prepared by template syntheses of the components.

Trioctahedrotetracarbazone copper dichloride ethanol (7) [L²CuCl₂]-EtOH: green solid; yield 68%; m.p. 180 °C; IR (KBr) 3403 (OH), 2099 (CNN), 1109, 627 (ClO₂), 1619 (CN), 761 (CS) cm⁻¹. UV/VIS: 315, 360, 855 nm.

Elemental analyses of C₄H₇N₂O₃SCuCl₂
Calcd C 22.88 H 3.16 N 24.65%,
Found C 22.68 H 3.15 N 24.80%.

Trioctahedrotetracarbazone copper dichloride monohydrate (9) [L³CuCl₂]-H₂O: green solid; yield 57%; m.p. 160 °C; IR (KBr) 3378 (OH), 3255 (NH₂) 2079 (enyl), 1700 (C =O), 1614 (C =O), 835 (C =S) cm⁻¹. UV/VIS: 300, 333, 830 nm.

Elemental analyses of C₄H₇N₂O₃CuCl₂
Calcd C 25.60 H 4.00 N 23.20%,
Found C 24.95 H 3.81 N 22.97%.

Triazolthiosemicarbazone copper dichloride monohydrate (10) [L⁴CuCl₂]-H₂O: green solid; yield 34%; m.p. 140 °C; IR (KBr) 3400 (OH), 3328 (NH₂) 1685 (C =O), 1659 (C =N) cm⁻¹. UV/VIS: 325, 340, 370, 790 nm.

Elemental analyses of C₄H₁₄N₂O₃CuCl₂
Calcd C 26.63 H 4.20 N 28.71%,
Found C 26.33 H 4.60 N 28.19%.

General procedure for the preparation of 11 and 12
To an ethanolic suspension (1.6 mmol) of the ligand (L³ and L⁴) a solution (0.8 mmol) of copper(II) perchlorate in EtOH was added. The mixture was stirred at room temperature (caution with perchlorates!) for two hours. The olive-green solid formed was filtered off, washed with ethanol and dried in vacuo.

Bis[2,8-dimethyl-5-thione-3,4,6,7,10,11,12-heptaazaacyclo[7.2.1]dodeca-2,7,11,12-tetraene] copper(II) diperchlorate trihydrate (11): olive-green solid; yield 66%; IR (KBr) 3392 (OH), 2099 (CNN), 1109, 627 (ClO₂), 1619 (CN), 761 (CS) cm⁻¹. UV/VIS: 415, 520, 880 nm.

Elemental analyses of C₁₈H₁₄N₄O₁₂S₂Cl₂
Calcd C 22.03 H 3.15 N 25.70%,
Found C 22.18 H 3.16 N 25.65%.
(2,8-Dimethyl-5-oxo-3,4,6,7,10,11,12-heptaazabicyclo[7.2.1]dodeca-2,7,11,12-tetraenato)copper(II) tetrahydrate (12): green solid; yield 46%; IR (KBr) 3418 (OH), 1685 (C = O), 1623 (C=N) cm$^{-1}$.

Elemental analyses of $C_9H_{17}N_7O_4Cu$

Calcd C 30.80 H 4.85 N 27.96%,
Found C 29.53 H 5.40 N 28.71%.

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