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

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Template 1:1 condensation of 3,5-diacetyl-1,2,4-triazole with thiocarbohydrazide or carbohydrazide in the presence 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 L₁, L₂, L₃, L₄, and closed [1+1] ligands (mesocyclic ligands) L⁵ and L⁶ 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 [CuLX₂] and [Cu⁺L²⁻] complexes.

All these compounds have been characterized by ¹H NMR, IR, electronic and mass spectra and by analytical data.

Results and Discussion

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 compounds 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 diazacycloundine 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 template [2+2] condensations and the isolation of various [1+1] open and cyclic ligands and their complexes.

We previously considered the synthesis of the ligands by the condensation of 3,5-diacetyl-1,2,4-triazole with thiocarbohydrazide (L₁), carbohydrazide (L₂), thiosemicarbazide (L₃) and semicarbazide (L₄). The same condensation reaction for...
thiocarbohydrazide and carbohydrazide in presence of LiOH yields the new mesocyclic [1+1] (L⁵) and (L⁶) 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 L⁷ and L⁸ 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 L² [16].

The analogous L¹ 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 L³ and L⁴. The EI mass spectrum of the L⁴ 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 L³ (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 L³ (1:1) and the 1:2 derivative, that does not modify the L³ microanalysis.

Due to the low solubility in common solvents, only the ¹H NMR in CD₃SOCD₃ of L³ and L⁵ have been recorded.

The sharp singlet signal at 15.0 ppm in the ¹H NMR spectrum of L³ has been assigned to the ionizable proton which has a strong interaction with the carbonyl group of the molecule [11].

The ¹H NMR spectrum of L⁵ differs slightly from that of L³, and clearly demonstrates the absence of an interaction of the ionizable proton, δ 12.5 ppm. Two sharp singlets at δ 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]
Fig. 1. Mass spectrum of L3.

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 persistant 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, thiocarbohydrazide, 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 were recorded in dimethylformamide solution were run in a Pye-Unicam Sp-8-100 spectrophotometer.¹ H NMR spectra were recorded on a Bruker WH-200 spectrometer in CD₂SOCD₃ 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 Investigacion (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, dried in vacuo, and recrystallized from ethanol.

Triazolthiocarbazone (L¹): yellow solid; yield 73%; m.p. 135 °C; IR (KBr) 3394, 3382 (N H₂), 1701 (C = O), 1616 (C=N), 799 (C=S) cm⁻¹.

Elemental analyses of C₁₁H₁₂N₁₂O₃ (241)
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 (NH₂), 1694 (C = O), 1625 (C=N) cm⁻¹.

Elemental analyses of C₁₁H₁₃N₁₂O₇ (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;¹ H NMR (DMSO-d₆) δ 14.98 (s, 1 H, NH triazol), 11.0 (s, 1 H, NH amine), 8.41 (s, 2 H, NH₂), 2.37, 2.32 (s, 3 H, 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 C₁₁H₁₄N₁₂O₄S (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⁺).

**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-di-acetyl-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 separated solid was collected by filtration, washed with ethanol, and dried in vacuo.

(2,8-Dimethyl-5-thione-3,4,6,7,10,11,12-heptaaazarabiclo[7.2.1]dodeca-2,7,11,12-tetraene)penta-hydrate (L⁵): yellow solid; yield 24%; m.p. 205 °C;¹ H NMR (DMSO-d₆) δ 12.52 (s, 1 H, NH triazol), 10.95, 10.12 (s, 1 H, NH amine), 2.49, 2.48 (s, 3 H, CH₃); IR (KBr) 3349 (OH), 3197 (NH), 1612 (C=N), 796 (C=S) cm⁻¹.

Elemental analyses of C₁₄H₁₉N₁₂O₃S (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-heptazabicyclo[7.2.1]dodeca-2,7,11,12-tetraene)tetra-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 C₁₄H₁₇N₁₂O₅ (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-di-acetyl-1,2,4-triazole (1.3 mmol) in EtOH was added. After addition of 1.3 mmol of thiocarbazide, thiosemicarbazide, carbazide or semicarbazide in EtOH/H₂O (1:1) the yellow products precipitated and were filtered off.

Bistriazolthiocarbazone lead dithiocyanate (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 C₁₃H₁₈N₁₂O₃S₂Pb
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%.

Triaizolbis(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=N), 1600 (C=O), 1571, 880 nm.

Elemental analyses of C14H24N4O4Pb
Calcd C 22.03 H 3.15 N 25.70%, Found C 22.18 H 3.16 N 25.65%.

Bistriazolcarbazone lead bisthiocyanate tetraethanol (3): orange solid; yield 86%; m.p. 140 °C; IR (KBr) 3443 (OH), 2052 (NCS), 1700, 1679 (C=O), 1619 (C=N) cm⁻¹.

Elemental analyses of C23H40N2O4Pb2
Calcd C 34.19 H 4.00 N 19.28 Pb 23.89%, Found C 33.95 H 4.00 N 19.28 Pb 23.25%.

Triazolsemicarbazone tetrahydrate (4); yellow solid; yield 15%; m.p. 262 °C; IR (KBr) 3465 (OH), 1700, 1679 (C=O), 1619 (C=N) cm⁻¹.

Elemental analyses of C14H24N4O2Pb2
Calcd C 22.95 H 2.83 N 22.30 Pb 35.96%, Found C 22.99 H 3.46 N 21.40 Pb 35.56%.

General procedure for the preparation of 5 and 6
To a suspension of complex 3 (1.2 mmol) in EtOH a solution of 1.2 mmol of carbazide or 1,3-diaminopropane was added to yield a precipitate which was filtered off.

(2,8,13,19-Tetramethyl-5,16-dioxo-3,4,6,7,10,11,14,15,17,18,21,22,23,24-tetradecaaza­tricyclo[18.2.19.12]tetracosa-2,7,11,13,18,22,23,24-octane)bis(lead dihydroxy) diethanol (5): yellow solid; yield 18%; m.p. 98 °C; IR (KBr) 2054 (NCS), 1659 (C=O), 1619 (C=N) cm⁻¹.

Elemental analyses of C23H32N18O8Pb2
Calcd C 22.95 H 2.83 N 22.30 Pb 35.96%, Found C 22.99 H 3.46 N 21.40 Pb 35.56%.

Triazolthiocarbazone copper dichloride diethanol (6); brown solid; yield 48%; m.p. 118 °C; IR (KBr) 3351 (OH), 2059 (enyl), 1655 (C=O), 1620 (C=N), 1185 (C=O) cm⁻¹.

Elemental analyses of C14H22N14O4Pb2
Calcd C 23.37 H 4.38 N 19.65 Pb 47.83%, Found C 23.30 H 4.18 N 19.55 Pb 46.94%.

General procedure for the preparation of 7–10
To an ethanolic suspension of the ligand (L1, L2, L3 or L4) a solution (1.6 mmol) of copper dichloride in EtOH was added; the mixture was stirred to 60 °C for 2 h. A green solid separated was filtered off, washed with ethanol, and dried in vacuo.

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

Triazolthiocarbazone copper dichloride ethanol (7) [L²CuCl₂]·EtOH: green solid; yield 68%; m.p. 180 °C; IR (KBr) 3403 (OH), 3403 (NH2), 2105 (enyl), 1700 (C=O), 1619 (C=N), 758 (C=S) cm⁻¹. UV/VIS: 315, 360, 855 nm.

Elemental analyses of C20H17N13O8SCuCl2
Calcd C 22.88 H 3.16 N 24.65%, Found C 22.68 H 3.15 N 24.80%.

Triazolthiocarbazone copper dichloride ethanol (8) [L²CuCl₂]·EtOH: green solid; yield 51%; m.p. 150 °C; IR (KBr) 3408 (OH), 1700 (C=O), 1632 (C=N) cm⁻¹. UV/VIS: 300, 800 nm.

Elemental analyses of C20H17N13O8CuCl2
Calcd C 25.60 H 4.00 N 23.20%, Found C 24.95 H 3.81 N 22.97%.

Triazolthiosemicarbazone copper dichloride monohydrate (9) [L²CuCl₂]·H₂O: green solid; yield 57%; m.p. 160 °C; IR (KBr) 3378 (OH), 3255 (NH2), 2079 (enyl), 1700 (C=O), 1614 (C=N), 835 (C=S) cm⁻¹. UV/VIS: 300, 333, 830 nm.

Elemental analyses of C20H17N13O8CuCl2

Triazolsemicarbazone copper dichloride monohydrate (10) [L²CuCl₂]·H₂O: green solid; yield 34%; m.p. 140 °C; IR (KBr) 3300 (OH), 3328 (NH2), 1685 (C=O), 1659 (C=N) cm⁻¹. UV/VIS: 325, 340, 370, 790 nm.

Elemental analyses of C20H17N13O8CuCl2
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 (L5 and L6) 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-heptadecaazabicyclo[7.2.1]dodeca-2,7,11,12-tetraene)-copper(II) diperchlorate trihydrate (11): olive-green solid; yield 66%; IR (KBr) 3592 (OH), 2099 (CNN), 1109, 627 (ClO₄), 1619 (CN), 761 (CS) cm⁻¹. UV/VIS: 415, 520, 880 nm.

Elemental analyses of C24H22N14O15S₂Cl₂
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-heptaa-
zbicyclo[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 C₉H₁₇N₇O₄Cu
Calcd C 30.80 H 4.85 N 27.96%
Found C 29.53 H 5.40 N 28.71%

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