Copper(II) Complexes of Hydrazone Derivatives

P. Souza*[a], M. A. Mendiola[a], A. Arquero[b], V. Fernández[a], E. Gutiérrez-Puebla[c], C. Ruiz-Valero[c]

[a] Departamento de Química (C−VIII), Facultad de Ciencias, Universidad Autónoma de Madrid, Cantoblanco, 28049-Madrid, Spain

[b] Departamento A.T.S.I., Facultad de Informática, Universidad Politécnica de Madrid, Montegancedo s/n, 28660-Boadilla del Monte, Madrid, Spain

[c] Instituto de Ciencias de Materiales, Sede D, CSIC. Serrano, 113, 28006-Madrid, Spain

Z. Naturforsch. **49b**, 263−271 (1994); received June 2/October 4, 1993

Benzil, Hydrazones, Copper(II), Macroligands, Crystal Structure

Three benzil based, macrocyclic oxygen-, nitrogen-, and sulfur-containing ligands, (3,4,10,11-tetraphenyl-1,2,5,6,8,9,12,13-octaazacyclotetradeca-7,14-dithione-2,4,9,11-tetraene) ethanol (L^1), 10,11-diethoxy-3,4,10,11-tetraphenyl-1,2,5,6,8,9,12,13-octaazacyclotetradeca-7,14-dithione-2,4-diene (L^2), (3,4,10,11-tetraphenyl-1,2,5,6,8,9,12,13-octaazacyclotetradeca-7,14-dione-2,4,9,11-tetraene) ethanol (L^3); a cyclic ligand, 6-ethoxy-1,6-diphenyl-4-oxo-3,4,5,6-tetrahydro-2,3,5-triazine (L^5) and two open chain ligands, benzilsemicarbazone (L^6) and benzilbisthiosemicarbazone (L^4) are reported. These ligands react with copper(II) chloride, nitrate and acetate. The complexes obtained have been characterized on the basis of NMR, IR, electronic and mass spectral studies, conductance and analytical data. The stoichiometry and the spectroscopic data of the complexes indicate that the copper ions are coordinated by neutral ligands or by ligand anions formed by loss of protons from the ligand.

The molecular and crystal structure of 6-ethoxy-1,6-diphenyl-4-oxo-3,4,5,6-tetrahydro-2,3,5-triazine (L^5) was determined by X-ray diffraction; the space group is triclinic, $P\bar{1}$ with $a = 7.865(1)$, $b = 14.101(6)$, $c = 15.733(9)$ Å, $\alpha = 69.10(3)°$, $\beta = 75.62(2)°$, $\gamma = 86.69(2)°$, $V = 1578(1)$ Å^3, $Z = 4$.

Introduction

Thiosemicarbazone and semicarbazone have been studied intensively due to their wide range of potential biological uses. Their metal complexes, especially those containing copper(II) and iron(II), are more active than the uncoordinated thiosemicarbazone molecules [1−4].

Schiff-base condensation and related processes have been frequently controlled by metal ion templates. In many cases it is difficult to design control experiments and test to distinguish different roles of the metal ions [5−7].

In the present paper we describe reactions of thiocarbohydrazide and semicarbazide with benzil, which give new macrocycle ligands L^1, L^2 and L^3, a cyclic ligand L^5 and an open chain ligand L^6. Benzilbisthiosemicarbazone L^4 was prepared as previously described in the literature [8,9]. All the ligands were synthesized without ion template effect. As reported, the activity of those free ligands is due to their complexation with copper ions [10]. Also their copper complexes cause considerable oxidative stress by cytotoxicity [11]. Therefore, the coordination chemistry of these new ligands with copper(II) salts were studied.

All compounds isolated were characterized by elemental analyses, IR, ^{1}H NMR, ^{13}C NMR, UV−V and mass spectroscopic studies.

The crystal and the molecular structure of L^5 has been determined by X-ray crystallography.

Experimental

Semicarbazide hydrochloride, thiosemicarbazide, carbohydrazide, thiocarbohydrazide, benzil, copper(II) chloride dihydrate, copper(II) nitrate pentahydrate and copper acetate were commercial products of highest chemical grade. Solvents were purified according to standard procedures.

IR spectra in the 4000−200 cm^{-1} range were recorded as KBr pellets on Bomen and Perkin Elmer 683 spectrophotometers. UV/V spectra in dimethylformamide solution were run on a Pye-Unicam SP-8-100 spectrophotometer. Conductivity data were measured using freshly prepared dimethylformamide solutions (*ca.* 10^{-3} M) at 25 °C with a Metrohm Herisau model E-518. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker WH-200 spectrometer system with TMS as the internal standard. Fast atom bombardment mass spectra were

---

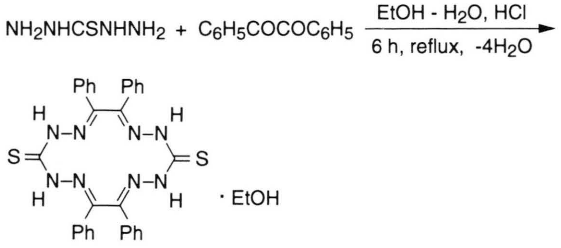
* Reprint requests to Prof. Dr. Pilar Souza.

Verlag der Zeitschrift für Naturforschung,
D-72072 Tübingen
0932−0776/94/0200−0263/$ 01.00/0

recorded on a VG Auto Spec using Cs^+ as fast atom and mNBA as the matrix.

Preparation of the ligands

[3,4,10,11-Tetraphenyl-1,2,5,6,8,9,12,13-octaazacyclotetradeca-7,14-dithione-2,4,9,11-tetraene] ethanol; L^1.

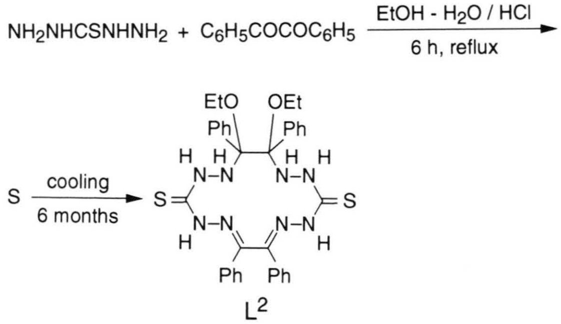

L^1

To a boiling ethanol-water (20:5 v/v) solution of thiocarbohydrazide (30 mmol) was added an ethanolic solution (30 ml) of benzil (30 mmol) with 1 ml of conc. HCl. The solution was refluxed for 6 h and allowed to stand for 24 h. A dark yellow solid was collected by filtration, m.p. 212 °C. The compound was slightly soluble in ethanol and $CHCl_3$.

$C_{32}H_{30}N_8OS_2$

Calcd	C 63.28	H 4.94	N 18.46%,
Found	C 62.96	H 4.70	N 18.48%.

[10,11-Diethoxy-3,4,10,11-tetraphenyl-1,2,5,6,8,9,12,13-octaazacyclotetradeca-7,14-dithione-2,4-diene]; L^2.

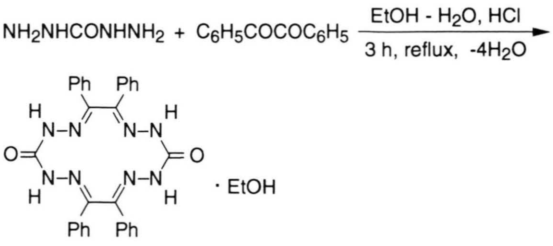

L^2

On cooling for six months of the remaining solution of the L^1 preparation a pale yellow crystalline product was obtained, m.p. 150 °C. The compound is soluble in $CHCl_3$ and alcohol.

$C_{34}H_{36}N_8O_2S_2$

Calcd	C 62.50	H 5.51	N 17.15%,
Found	C 62.10	H 5.50	N 17.11%.

[3,4,10,11-Tetraphenyl-1,2,5,6,8,9,12,13-octaazacyclotetradeca-7,14-dione-2,4,9,11-tetraene] ethanol; L^3.

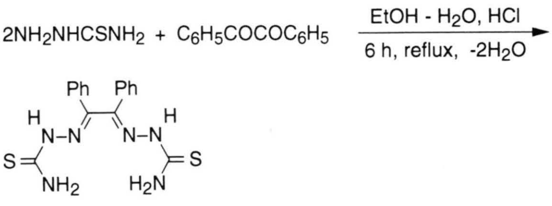

L^3

To a boiling ethanol-water (20:5 v/v) solution of carbohydrazide (30 mmol) was added an ethanolic solution (30 ml) of benzil (30 mmol) with 1 ml of conc. HCl. The solution was refluxed for 30 min and a gum-like solid formed. The gum was kept stirring and refluxing in ethanol for several hours. The yellow solid formed was broken, filtered off, washed and recrystallized from EtOH, m.p. 232 °C. The product is soluble in $CHCl_3$ and slightly soluble in EtOH.

$C_{32}H_{30}N_8O_3$

Calcd	C 66.83	H 5.22	N 19.49%,
Found	C 66.40	H 4.99	N 19.39%.

Benzilbisthiosemicarbazone[8]; (L^4).


L^4

A solution of benzil (20 mmol) in ethanol (20 ml) was added to a boiling ethanol-water (20:5 v/v) suspension of thiosemicarbazide (40 mmol), followed by the addition of 1 ml conc. HCl. The reaction mixture was refluxed for 6 h. The yellow solid formed was filtered off, washed with aqueous ethanol and dried *in vacuo* (75%), m.p. 241 °C. The compound is slightly soluble in ethanol and $CHCl_3$.

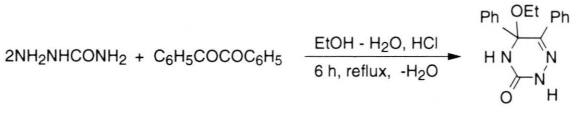
$C_{16}H_{16}N_6S_2$

Calcd	C 53.93	H 4.59	N 23.08%,
Found	C 54.15	H 4.49	N 23.59%.

MS(THF): $m/z(\%) = 357.0(46)\ (M^+ + 1)$.

This compound was also obtained by the following procedure [9]: The thiosemicarbazide (40 mmol) was dissolved in 40 ml of methanol, 40 ml of 2 N HCl and 1 ml of conc. HCl, and then added to a suspension of benzil (20 mmol) in 50 ml of methanol and some drops of conc. HCl. The mixture was stirred for 6 h at room temperature, the yellow solid filtered off, washed with methanol and dried *in vacuo*. The analytical data agree with the proposed formula.

6-Ethoxy-1,6-diphenyl-4-oxo-3,4,5,6-tetrahydro-2,3,5-triazine; L^5.



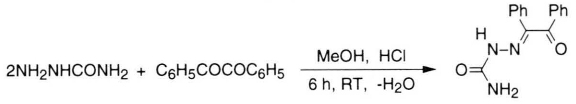
L^5

A solution of benzil (20 mmol) in ethanol (20 ml) was added to a boiling ethanol-water solution (20 : 5 v/v) of semicarbazide (40 mmol) and 1 ml of conc. HCl. The solution was refluxed for 6 h. A white crystalline solid formed overnight, which was filtered off, washed with aqueous ethanol and dried *in vacuo* (70%) m.p. 225 °C.

$C_{17}H_{17}N_3O_2$

Calcd	C 69.15	H 5.76	N 14.23%,
Found	C 68.95	H 5.61	N 14.19%.

Benzilsemicarbazone, (L^6).



L^6

This compound was obtained under the same conditions described for L^4 in the second procedure. The yellowish-white solid was collected by filtration, washed with methanol and dried *in vacuo* (60%), m.p. 160 °C. The compound is slightly soluble in ethanol and chloroform.

$C_{15}H_{13}N_3O_2$

Calcd	C 67.41	H 4.94	N 15.73%,
Found	C 67.15	H 4.62	N 15.44%.

MS (THF): $m/z(\%) = 268(95)\ (M^+ + 1),\ 105(57)\ (M^+ + 1 - 163)$.

Preparation of the complexes

[3,4,10,11-Tetraphenyl-1,2,5,8,9,12,13-octaaza-cyclo-tetradeca-7,14-dithione-2,4,9,11-tetraenide]-dicopper(II) diethanol (7) $[(L^1)^{4-}(Cu^{2+})_2]\ (EtOH)_2$.

To a boiling ethanol suspension of L^1 (2 mmol) was added an ethanolic solution of copper(II) chloride dihydrate (2 mmol). After three hours a brown powder was isolated from the yellow-green solution, m.p. 228 °C.

$C_{34}H_{32}N_8Cu_2OS_2$

Calcd	C 52.59	H 4.12	N 14.73%,
Found	C 52.87	H 4.08	N 14.44%.

Λ_M, 30.22 ohm^{-1} cm^2 mol^{-1}. λ_{max}/nm (DMF) 355, 655 and 850. This complex was also obtained at room temperature using a $CHCl_3-EtOH$ solution of L^1 and an EtOH solution of copper salt.

[3,4,10,11-Tetraphenyl-1,2,5,8,9,12,13-octaaza-cyclotetradeca-7,14-dithione-2,4,9,11-tetraene]-dichlorocopper(II) hexahydrate (**8**) $[(L^2)CuCl_2]\ (H_2O)_6$.

This complex can be prepared by two different synthetic procedures. Either by addition of a $CuCl_2 \cdot 2H_2O$ (2 mmol) ethanolic solution to a solution of L^2 (2 mmol) in chloroform-ethanol (1 : 2 v/v) at room temperature or by cooling the green remaining solution of the preceding synthesis of 7. The lustrous green solid was isolated by filtration, m.p. 212–215 °C.

$C_{30}H_{36}N_8Cl_2CuO_6S_2$

Calcd	C 44.86	H 4.49	N 13.95%,
Found	C 44.60	H 4.47	N 13.70%.

Λ_M, 14.50 ohm^{-1} cm^2 mol^{-1}. λ_{max}/nm (DMF) 320, 370 and 840.

[3,4,10,11-Tetraphenyl-1,2,5,6,8,9,12,13-octa-azacyclotetradeca-7,14-dithione-2,4,9,11-tetra-enide]copper(II)-nitrateethanol (**9**) $[(L^1)^{1-}(Cu^{2+})](NO_3)(EtOH)$.

To a methanolic suspension of L^1 (2 mmol) was added a methanolic solution of copper(II) nitrate pentahydrate (2 mmol) at room temperature. A dark solid precipitated from the green solution, m.p. 214 °C.

$C_{32}H_{29}H_9CuO_4S_2$

Calcd	C 52.51	H 3.96	N 17.23%,
Found	C 52.39	H 3.75	N 16.89%.

Λ_M, 71.82 ohm^{-1} cm^2 mol^{-1}. λ_{max}/nm (DMF) 310, 470 and 850.

[3,4,10,11-Tetraphenyl-1,2,5,6,8,9,12,13-penta-azacyclotetradeca-7,14-dione-2,4,9,11-tetraenide]-copper(II) ethanol (**10**) $[(L^3)^{2-}(Cu^{2+})](EtOH)$.

A similar procedure to the one described for **7** was used with L^3. A brown pale powdery precipitate was isolated, m.p. 230 °C.

$C_{32}H_{28}N_8CuO_3$

Calcd	C 60.37	H 4.40	N 17.61%,
Found	C 60.93	H 4.41	N 17.51%.

Λ_M, 10.93 ohm^{-1} cm^2 mol^{-1}. λ_{max}/nm (DMF) 270, 425, 480 (sh) and 850.

[3,4,10,11-Tetraphenyl-1,2,5,6,8,9,12,13-octaazacyclotetradeca-7,14-dione-2,4,9,11-tetraenide]-copper(II)-nitrateethanol (**11**)
$[(L^3)^{1-}(Cu^{2+})](NO_3)(EtOH)$.

A similar procedure to the one described for **9** was used with L^3. A brown solid was isolated, m.p. 220 °C.

$C_{32}H_{29}N_9CuO_6$
Calcd C 54.93 H 4.15 N 18.02%,
Found C 55.11 H 4.05 N 17.83%.

Λ_M, 69.73 ohm^{-1} cm^2 mol^{-1}.

[3,4,10,11-Tetraphenyl-1,2,5,6,8,9,12,13-octaazacyclotetradeca-7,14-dithione-2,4,9,11-tetraenide]-copper(II) ethanol-hydrate (**12**)
$[(L^1)^{2-}(Cu^{2+})](EtOH)(H_2O)$.

An ethanolic suspension of L^1 (2 mmol) and copper(II) acetate (1 mmol) was refluxed for 20 h. The brown solid was filtered off, washed with ethanol and dried *in vacuo*, m.p. 248 °C.

$C_{32}H_{30}N_8CuO_2S_2$
Calcd C 55.95 H 4.37 N 16.32%,
Found C 56.23 H 4.27 N 15.89%.

Λ_M, 1.5 ohm^{-1} cm^2 mol^{-1}. λ_{max}/nm (DMF) 335, 520 and 565.

(Benzilbisthiosemicarbazonide)copper(II) (**13**)
$[(L^4)^{2-}(Cu^{2+})]$

An ethanolic solution of copper(II) chloride dihydrate (2 mmol) was added to a suspension of L^4 (4 mmol) in ethanol at room temperature. The reaction mixture was kept stirring for 5 h, the reddish-brown solid formed was filtered off, washed with ether and dried *in vacuo*, m.p. 208 °C.

$C_{16}H_{14}N_6CuS_2$
Calcd C 45.98 H 3.35 N 20.11%,
Found C 45.87 H 3.39 N 19.87%.

Λ_M = 46.5 ohm^{-1} cm^2 mol^{-1}. λ_{max}/nm (DMF) 317, 502 and 550 (sh). MS(THF): m/z(%) = 418(72) (M$^+$ + 1).

Bis(benzilbisthiosemicarbazone)copper(II) dinitrate (**14**) $[(L^4)_2Cu(NO_3)_2]$

The reddish-brown nitrate complex was obtained by an analogous way described for the chloride derivative, m.p. 250 °C.

$C_{32}H_{32}N_{14}CuO_6S_4$
Calcd C 42.88 H 3.13 N 18.76%,
Found C 43.09 H 3.05 N 18.60%.

Λ_M = 15.5 ohm^{-1} cm^2 mol^{-1}. λ_{max}/nm (DMF) 313, 500 and 550 (sh).

(Benzilbisthiosemicarbazonide)dicopper(II) (**15**)
$[(L^4)^{4-}(Cu^{2+})_2]$

This compound was obtained under the same conditions as described for 12. A dark red precipitate was isolated, m.p., 234 °C.

$C_{16}H_{12}N_6Cu_2S_2$
Calcd C 40.08 H 2.50 N 17.53%,
Found C 40.68 H 2.80 N 17.18%.

Λ_M = 2.0 ohm^{-1} cm^2 mol^{-1}. λ_{max}/nm (DMF) 300, 350, 545 and 600 (sh).

μ-Diacetato-di(6-ethoxy-1,6-diphenyl-4-oxo-3,4,5,6-tetrahydro-2,3,5-triazine)dicopper(II) (**16**)
$[(L^5)_2Cu_2(C_2H_3O_2)_4]$

An ethanolic solution of L^5 (2 mmol) was added to an ethanolic copper(II) acetate suspension (1 mmol) and a few drops of piperidine. The mixture was refluxed for 2 h. A brown solution was obtained, which was concentrated slowly until a brown solid formed. The solid product was filtered off and finally dried *in vacuo*, m.p. 192 °C.

$C_{42}H_{46}N_6Cu_2O_{12}$
Calcd C 52.88 H 4.83 N 8.81%,
Found C 52.44 H 5.07 N 9.20%.

Λ_M, 3.0 ohm^{-1} cm^2 mol^{-1}. λ_{max}/nm (DMF), 350, 450, 600.

X-ray structure determination

A summary of the crystal structure data is given in Table I. A prismatic colourless crystal was mounted on a four-circle diffractometer. Exact cell dimensions were refined by least-squares methods on the Bragg angles of 25 carefully centered reflections.

The intensities were corrected for Lorentz and polarizations effects. Scattering factors for neutral atoms were taken from the International Tables for X-Ray Crystallography [12]. The structure was solved by direct methods [13] and Fourier syntheses.

The final refinement was made with anisotropic thermal parameters for the non-hydrogen atoms and fixed isotropic thermal parameters and coordinates for the H atoms.

Most of the calculations were carried out with the X-Ray 80 systems [14]. Table II contains the atomic parameter*.

---

* Further details may be obtained from: Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, by quoting the Registry-No. CSD 57738, the names of the authors and the journal citation.

Table I. Crystal structure data for $C_{17}H_{17}N_3O_2$.

Formula	$C_{17}H_{17}N_3O_2$
fw	296.3
crystal system	triclinic
space group	$P\bar{1}$
a [Å]	7.865(1)
b [Å]	14.101(6)
c [Å]	15.733(9)
α [°]	69.10(3)
β [°]	75.62(2)
γ [°]	86.69(2)
V [Å^3]	1578(1)
Z	4
F(000)	628
d(calcd), g cm^{-3}	1.25
Temp. [°C]	22
μ [cm^{-1}]	0.78
Cryst size [mm]	0.65 × 0.30 × 0.15
Diffractometer	Enraf-Nonius CAD4
Radiation	graphite-monochromated MoKα ($\lambda = 0.71069$ Å)
Scan technique	$\Omega/2\theta$
Data collected	(−9, −16,0) to (9,16,18)
rflns collected	5550
Unique data (I)≥2σ(I)	2602
std rflns	3 rflns
R [%]	4.3
R_w [%]	4.2
Average shift/error	0.003

Table II. Fractional atomic coordinates and equivalent isotropic displacement parameters for $C_{17}H_{17}N_3O_2$. $U_{eq} = 1/3\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* a_i \cdot a_j \cdot 10^3$.

Atom	x/a	y/b	z/c	U_{eq}
O 1	0.0783(3)	0.3796(2)	0.9906(2)	46(1)
O 2	−0.0768(3)	0.1309(2)	1.2679(2)	46(1)
C 1	−0.2650(5)	0.2766(3)	1.2417(2)	41(2)
N 2	−0.2334(4)	0.3721(2)	1.1987(2)	48(1)
N 3	−0.1116(4)	0.4048(2)	1.1137(2)	50(1)
C 4	−0.0248(5)	0.3430(3)	1.0697(3)	41(2)
N 5	−0.0564(4)	0.2436(2)	1.1143(2)	42(1)
C 6	−0.1749(5)	0.1948(3)	1.2061(2)	42(2)
C 7	0.0538(6)	0.1811(3)	1.2875(3)	63(2)
C 8	0.1413(7)	0.1007(4)	1.3534(4)	84(3)
C 11	−0.3048(5)	0.1268(3)	1.1960(2)	45(2)
C 12	−0.4157(6)	0.1718(3)	1.1382(3)	73(2)
C 13	−0.5318(7)	0.1131(5)	1.1229(4)	92(3)
C 14	−0.5377(8)	0.0093(5)	1.1662(4)	96(3)
C 15	−0.4304(8)	−0.0355(4)	1.2245(4)	92(3)
C 16	−0.3126(6)	0.0225(3)	1.2393(3)	64(2)
C 21	−0.4014(5)	0.2485(3)	1.3324(3)	50(2)
C 22	−0.5251(6)	0.3184(3)	1.3468(3)	69(2)
C 23	−0.6506(6)	0.2964(4)	1.4325(4)	85(3)
C 24	−0.6498(7)	0.2040(4)	1.5029(3)	84(3)
C 25	−0.5288(7)	0.1342(4)	1.4894(3)	72(2)
C 26	−0.4038(5)	0.1548(3)	1.4044(3)	57(2)
O 1	0.0723(4)	0.1159(2)	1.0095(2)	54(1)
O 2	0.1201(3)	0.3790(2)	0.7347(2)	49(1)
C 1	−0.0527(5)	0.2277(3)	0.7616(3)	43(2)
N 2	−0.0571(4)	0.1319(2)	0.8054(2)	55(2)
N 3	−0.0209(5)	0.0961(2)	0.8920(2)	60(2)
C 4	0.0355(5)	0.1543(3)	0.9320(3)	46(2)
N 5	0.0488(4)	0.2542(2)	0.8842(2)	43(1)
C 6	−0.0129(5)	0.3067(3)	0.7994(2)	40(2)
C 7	0.2847(6)	0.3379(4)	0.7034(3)	72(2)
C 8	0.4135(7)	0.4237(5)	0.6488(4)	132(4)
C 11	−0.1720(5)	0.3653(3)	0.8248(3)	43(2)
C 12	−0.3324(6)	0.3136(4)	0.8697(3)	69(2)
C 13	−0.4765(7)	0.3618(5)	0.9037(4)	94(3)
C 14	−0.4624(8)	0.4598(6)	0.8959(4)	99(4)
C 15	−0.3047(9)	0.5128(4)	0.8521(5)	102(4)
C 16	−0.1582(6)	0.4654(4)	0.8162(3)	72(2)
C 21	−0.0927(5)	0.2603(3)	0.6673(3)	47(2)
C 22	−0.1015(6)	0.3613(3)	0.6128(3)	58(2)
C 23	−0.1392(6)	0.3875(4)	0.5260(3)	68(2)
C 24	−0.1674(6)	0.3132(5)	0.4934(3)	79(3)
C 25	−0.1567(7)	0.2129(4)	0.5464(4)	89(3)
C 26	−0.1186(6)	0.1857(3)	0.6331(3)	68(2)

Results and Discussion

Stable N, O and S-donor Schiff base macrocycle ligands (L^1, L^2 and L^3) have been isolated from direct condensation of benzil with carbohydrazide and thiocarbohydrazide in presence of some drops of conc. HCl, in absence of metal ion as template in moderate to good yields. The condensation of benzil with semicarbazide and thiosemicarbazide under the same conditions yielded open chair ligands (L^4 and L^6) and the mesocyclic L^5. The microcrystalline compounds had elemental analyses consistent with the formulation given. White crystals of L^5 were grown by slow evaporation of a EtOH solution.

Figure 1 shows an ORTEP[15] view of the two independent, but similar molecules with their intermolecular hydrogen bonds between N 5′ ··· O 1 and N 5 ··· O 1′, with distances of 2.876(5) and 2.825(5) Å, respectively, and another intermolecular interaction between O 1 ··· N $3'^{(x,1-y,2-z)}$ and O 1′ ··· N $3^{(-x,-y,2-z)}$, at 2.868(4) and 2.814(4) Å, respectively. The 6-membered ring formed is almost planar with maximal deviations from the least-square plane of −0.05 Å for the N 3 and 0.15 Å for N 5′. The angle between the phenyl planes are 84.3° and 92.7° for the quoted molecules. This could be due to the position of the EtOH molecule iserted in the lattice. Table III summarizes important bond lengths and angles.

As shown in the Figure an ethanolate group is bonded to the C 6 atom of the new heterocycle formed in the reaction. This results may be explained in terms of an EtOH addition across one

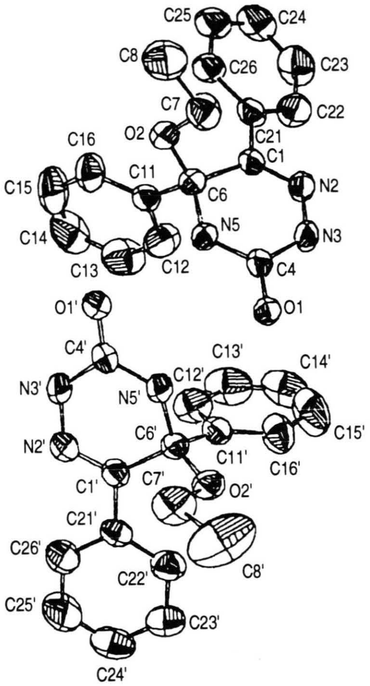


Fig. 1. ORTEP view of $C_{17}H_{17}N_3O_2$ (Ligand L^5).

of the azomethine linkages formed in a previous step, with a simultaneous elimination of a water molecule.

The ^1H and ^{13}C NMR data of the ligands obtained in $CDCl_3$ and/or $(CD_3)_2SO$ solution are given in Table IV and V.

The ^1H NMR spectra of L^5 and L^2 show characteristic signals of methyl and methylene groups of the ethanol molecule inserted, and a total absence of NH_2 signals.

The presence of the characteristic signal of OH group in the spectra of L^1 and L^3 confirms the existence of EtOH molecules of crystallization.

For the thio compounds, the data support the presence of thione tautomers in solution, with chemical shifts consistent with an imido (NH) (*ca.* 8−11 ppm) rather than a thiol (3−4 ppm) group [16].

The ^{13}C NMR spectra of the ligands exhibit signals at *ca.* 140 ppm assignable to imino carbon atoms indicating condensation; only the L^6 spectrum shows a peak assignable to a carbonyl group of the benzil moeity. The spectra of L^2 and L^5 show chemical shifts in the range 86−88 ppm, consistent

Table III. Selected bond lenghts (Å) and angles (°) for $C_{17}H_{17}N_3O_2$.

O1−C4	1.250(4)	O1′−C4′	1.245(5)
O2−C6	1.420(4)	O2′−C6′	1.422(4)
O2−C7	1.432(6)	O2′−C7′	1.433(5)
C1−N2	1.280(4)	C1′−N2′	1.277(5)
C1−C6	1.522(6)	C1′−C6′	1.516(6)
C1−C21	1.493(5)	C1′−C21′	1.497(6)
N2−N3	1.376(4)	N2′−N3′	1.370(5)
N3−C4	1.353(5)	N3′−C4′	1.347(6)
C4−N5	1.331(4)	C4′−N5′	1.335(4)
N5−C6	1.457(4)	N5′−C6′	1.463(5)
C6−C11	1.514(6)	C6′−C11′	1.509(5)
C7−C8	1.503(7)	C7′−C8′	1.482(7)
C6−O2−C7	115.8(4)	C6′−O2′−C7′	115.6(4)
C6−C1−C21	120.5(4)	C6′−C1′−C21′	120.0(4)
N2−C1−C21	114.9(4)	N2′−C1′−C21′	115.5(4)
N2−C1−C6	124.5(4)	N2′−C1′−C6′	124.5(4)
C1−N2−N3	118.8(4)	C1′−N2′−N3′	118.9(4)
N2−N3−C4	124.6(4)	N2′−N3′−C4′	124.7(4)
O1−C4−N3	120.3(4)	O1′−C4′−N3′	121.1(4)
N3−C4−N5	116.8(4)	N3′−C4′−N5′	116.4(4)
O1−C4−N5	122.8(4)	O1′−C4′−N5′	122.5(4)
C4−N5−C6	126.3(4)	C4′−N5′−C6′	126.0(4)
C1−C6−N5	108.8(4)	C1′−C6′−N5′	108.0(4)
O2−C6−N5	108.9(3)	O2′−C6′−N5′	108.0(3)
O2−C6−C1	111.7(3)	O2′−C6′−C1′	112.7(3)
N5−C6−C11	108.2(3)	N5′−C6′−C11′	108.2(3)
C1−C6−C11	112.2(4)	C1′−C6′−C11′	112.7(4)
O2−C6−C11	106.9(3)	O2′−C6′−C11′	107.1(3)
O2−C7−C8	107.3(4)	O2′−C7′−C8′	107.9(5)

Table IV. ^{1}H and ^{13}C NMR chemical shifts (ppm) of L^1, L^2 and L^3.

	L^1	L^2	L^3
CH_3	1.16 t	1.25 t	1.16 t
CH_2	3.62 c	3.45 c	3.63 c
OH	4.50 s		4.01 s
NH		4.51 s	
CH(Ph)	7.14–8.04 m	7.08–7.59 m	7.14–7.97 m
NH	9.90 s	10.04 s	9.50–10.50 m
NH	10.72 s		
NH	10.90 s		
CH_3	18.14	14.65	18.10
CH_2C-N	57.98	59.96	58.03
C–N		87.92	
Ph	126.52–131.52	125.84–129.37	125.01–129.60
C–C(Ph)		133.02	
C=N	141.00	138.91	132.00
C=N	149.00	144.48	134.00
C=X (X = S or O)	175.00	171.45	160.00

Table V. ^{1}H and ^{13}C NMR chemical shifts (ppm) of L^4, L^5 and L^6.

	L^4	L^5	L^6
CH_3		1.2 t	
CH_2		3.5 c	
NH	5.0 s	5.4 s	5.1 s
NH	6.1 s		6.0 s
CH(Ph)	7.2–7.9 m	7.1–7.6 m	7.2–7.9 m
NH	8.4 s	8.3 m	8.4 s
CH_3		15.02	
CH_2		57.80	
C–N		86.08	
Ph	126.76–130.18	126.75–128.35	126.01–132.10
C–C(Ph)	133.10	134.42	134.10
C=N	140.50	142.59	143.36
C=X (X = S or O)	179.08	149.04	156.33
C=O(benzil)			195.02

with saturation of the imino groups as resulting from EtOH insertion.

In the mass spectra of L^4 and L^6 the highest mass peak at m/z = 357 (46%) and m/z = 268 (97%), respectively, confirm the molecular weights. Daughter ions of these species correspond to the fragment ion m/z = 105 (57%) C_6H_5-CO- of L^6 spectrum.

The mass spectrum of complex 13 shows a parent peak at m/z = 418 (72%) supporting the formula proposed [17].

The stoichiometries of the complexes appear to indicate that copper is coordinated by the neutral ligands in 8, 14 and 16, and by the anions formed by loss of protons of the ligand in 7, 9, 10, 11, 12, 13 and 15.

All copper complexes are stable to air and moisture. The macrocyclic complexes 7, 8, 10 and 12, the open chain complexes 13, 14 and 15, and the L^5 complex, 16, are non-electrolytes, but 9 and 11 are 1:1 electrolytes owing to partial liberation of HNO_3.

The IR spectral data are summarized in Table VI. The ligand bands are consistent with the functional groups present in the molecules [16].

In the IR spectra of L^2 and L^4 complexes (8, 13,

Table VI. Selected IR bands (cm^{-1}) of the ligands and copper(II) complexes.

	$\nu(\text{NH})$ + $\nu(\text{NH}_2)$	$\nu(\text{C}\doteq\text{N}\doteq\text{N})^-$	$\nu(\text{C=N})$ + $\delta(\text{NH}_2)$	$\nu(\text{CO})$ (Benzil)	Amide I or Thioamide I	Thioamide IV
L^1	3323 3267	–	1597	–	1495	940
L^2	3240	–	1610	–	1495	970
L^3	3318 3817	–	1596	–	1713	–
L^4	3420 3330 3250 3150	–	1610	–	1465	840
L^5	3214 3075	–	1690	–	1700	–
L^6	3480 3198	–	1700 1580	1681	1705	–
7	–	2100	1590	–	1495	940
8	3260	–	1600	–	1480	880
9	–	2120	1590	–	1495	940
10	3310	–	1600	–	1720	–
11	3320	–	1590	–	1720	–
12	3266	2130	1663	–	1479	946
13	3440 3420	–	1620 1605	–	1435	815
14	3440	–	1620	–	1415	820
15	3446 3270 3101	–	1621 1600	–	1490 1456	786
16	3329 3208	–	1730	–	1661	–

14 and 15) the bands attributable to the thioamide I and IV stretching modes are split and shifted, which indicates that the sulphur and nitrogen atoms are involved in the coordination of copper [18]. The changes observed in the IR spectra of L^1 and L^3 complexes (7, 9, 10, 11 and 12) agree with copper nitrogen interaction, which is confirmed for the L^1 complexes (7, 9 and 12) by the new band assigned to $\nu\,(\text{C}\doteq\text{N}\doteq\text{N})^-$ vibration of the "enyl" form[19] of the ligand. The IR bands attributable to the NO_3^- ion modes are not visible due to overlapping with other ligand bands in the corresponding ranges.

The acetate complexes show two different patterns: the IR spectrum of 16 shows the acetate bridge bands at 2932, 2850, 1579 and 1423 cm^{-1}; in the spectra of 12 and 15 the acetate stretching modes disappear, which is evidence for loss of HAc upon complexation.

The electronic spectra of the 8, 9, 10, 12, 13, 14 and 15 show bands consistent with a distorted tetrahedral geometry at the metal ion. The spectrum of 7 shows a significant band at 655 nm usually found for square planar Cu(II) complexes[20]. The electronic spectrum of 16 shows a band at 600 nm which supports a di-nuclear structure as suggested by the IR data.

We thank the Dirección General de Investigación Científica y Técnica (Spain) for financial support (project PB 90−0227−C02−01).

[1] D. X. West, D. L. Huffman, J. Saleda, A. L. Liberta, Trans. Met. Chem. **16,** 565 (1991) and refs. therein.

[2] P. Pérez-Dubois, P. Souza, J. R. Masaguer, A. Arquero, Trans. Met. Chem. **12,** 200 (1987).

[3] P. Souza, L. Sanz, V. Fernández, A. Arquero, E. Gutiérrez, A. Monge, Z. Naturforsch. **46b,** 767 (1991).

[4] I. Haiduc, C. Silvestru, Coord. Chem. Rev. **99,** 253 (1990).

[5] D. H. Busch, N. A. Stephenson, Coord. Chem. Rev. **100,** 119 (1990).

[6] L. F. Lindoy, Chemistry of Macrocyclic Ligand Complexes; Cambridge University Press, Cambridge (1989).

[7] B. Dietrich, P. Viout, J. M. Lehn, Macrocyclic Chemistry, Weinheim, New York (1993).

[8] M. K. Pandey, O. P. Pandey, S. K. Sengupta, S. C. Triphati, Polyhedron **6,** 1611 (1987).

[9] G. R. Gummerus, C. A. **67,** 63894y (1967).

[10] a) W. E. Antholine, P. Gunn, L. E. Hopwood, Int. J. Radiat. Oncology Biol. Phys. **7,** 491 (1981);
b) H. G. Petering, H. H. Buskirk, J. A. Crim, G. J. Giessen, Pharmacologist **5,** 271 (1963);
c) C. F. Bell, K. A. K. Lott, N. Hearn, Polyhedron **6,** 1, 39 (1987).

[11] a) R. W. Byrnes, M. Mohan, W. E. Antholine, R. X. Xu, D. H. Petering, Biochemistry **29(30),** 7046 (1990);
b) A. Kraker, S. Krezoski, J. Schneider, D. Minkel, D. H. Petering, J. Biol. Chem. **260(25),** 13720 (1985).

[12] International Tables for X-Ray Crystallography, Vol. IV, Kynoch-Press, Birmingham, U.K. (1974).

[13] P. Main, S. J. Fiske, S. E. Hull, L. Lessinger, G. Germain, J. P. Declercq, M. M. Woolfson, MULTAN 80, University of York, U. K. (1980).

[14] J. K. Stewart, The X-Ray System, Computer Science Center, University of Maryland, College Park (1980).

[15] C. K. Johnson, ORTEP, Oak Ridge National Laboratory Report N° ORNL-3794, Tennessee (1985), unpublished.

[16] E. S. Raper, Coord. Chem. Rev. **61,** 115 (1985).

[17] R. S. Drago, Physical Methods in Chemistry, W. B. Saunders Company, Philadelphia (1977).

[18] S. Padhey, G. P. Kauffman, Coord. Chem. Rev. **63,** 127 (1985).

[19] N. B. Colthup, L. H. Daly, S. E. Wiberley, Introduction to Infrared and Raman Spectroscopy, 3nd. Ed., Academic Press, Boston (1990).

[20] a) A. B. P. Lever, Inorganic Electronic Spectroscopy 2nd, Ed., Elsevier, Amsterdam (1984);
b) B. J. Hathaway, Structure and Bonding **57,** 55 (1984).