Copper(II) Complexes of Hydrazone Derivatives

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

Benzil, Hydrazone, 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 (L1), 10,11-diethoxy-3,4,10,11-tetraphenyl-1,2,5,6,8,9,12,13-octaazacyclotetradeca-7,14-dithione-2,4-diene (L2), (3,4,10,11-tetraphenyl-1,2,5,6,8,9,12,13-octaazacyclotetradeca-7,14-dione-2,4,9,11-tetraene) ethanol (L3); a cyclic ligand, 6-ethoxy-1,6-diphenyl-4-oxo-3,4,5,6-tetrahydro-2,3,5-triazine (L5) and two open chain ligands, benzilsemicarbazone (L6) and benzilbisthiosemicarbazone (L4) 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 the crystal structure of 6-ethoxy-1,6-diphenyl-4-oxo-3,4,5,6-tetrahydro-2,3,5-triazine (L5) was determined by X-ray diffraction; the space group is triclinic, P 1  with $a = 7.865(1)$, $b = 14.101(6)$, $c = 15.733(9)$ Å, $\alpha = 69.10(3)^\circ$, $\beta = 75.62(2)^\circ$, $\gamma = 86.69(2)^\circ$, $V = 1578(1)$ 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 L1, L2 and L3, a cyclic ligand L5 and an open chain ligand L6. Benzilbisthiosemicarbazone L4 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 L5 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

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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**

\[\text{[3,4,10,11-Tetraphenyl-1,2,5,6,8,9,12,13-octaaza-cyclotetradeca-7,14-dione-2,4,9,11-tetraene]}\] ethanol; L1.

\[
\text{NH}_2\text{NHCONHNH}_2 + \text{C}_6\text{H}_5\text{COCO}_2\text{H}_5 \rightarrow \text{EtOH - H}_2\text{O}, \text{HCl} \rightarrow 6 \text{h, reflux, } -4\text{H}_2\text{O}
\]

\[L^1\]

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 CHCl3.

\[\text{C}_{32}\text{H}_{30}\text{N}_8\text{O}_3\text{S}_2\]

Calcd C 63.28 H 4.94 N 18.46%,

Found C 62.96 H 4.70 N 18.48%.

\[\text{[10,11-Diethoxy-3,4,10,11-tetraphenyl-1,2,5,6,8,9,12,13-octaazacyclotetradeca-7,14-diene]}\]; L2.

\[
\text{NH}_2\text{NHCSNH}_2 + \text{C}_6\text{H}_5\text{COCO}_2\text{H}_5 \rightarrow \text{EtOH - H}_2\text{O}, \text{HCl} \rightarrow 6 \text{h, reflux, } -4\text{H}_2\text{O}
\]

\[L^2\]

On cooling for six months of the remaining solution of the L1 preparation a pale yellow crystalline product was obtained, m.p. 150 °C. The compound is soluble in CHCl3 and alcohol.

\[\text{C}_{32}\text{H}_{30}\text{N}_8\text{O}_3\text{S}_2\]

Calcd C 62.50 H 5.51 N 17.15%,

Found C 62.10 H 5.50 N 17.11%.

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 CHCl3.

\[\text{C}_{16}\text{H}_{16}\text{N}_5\text{S}_2\]

Calcd C 53.93 H 4.59 N 23.08%,

Found C 54.15 H 4.49 N 23.59%.

Benzilbisthiosemicarbazone\(^5\); (L4).

\[
\text{2NH}_2\text{NHCSNH}_2 + \text{C}_6\text{H}_5\text{COCO}_2\text{H}_5 \rightarrow \text{EtOH - H}_2\text{O}, \text{HCl} \rightarrow 6 \text{h, reflux, } -2\text{H}_2\text{O}
\]

\[L^4\]

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 CHCl3 and slightly soluble in EtOH.

\[\text{C}_{32}\text{H}_{30}\text{N}_8\text{O}_3\]

Calcd C 66.83 H 5.22 N 19.49%,

Found C 66.40 H 4.99 N 19.39%.

Unauthenticated
Download Date | 5/23/19 1:13 AM
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 2N 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; L⁵.

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. HCI. 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_{31}N_{8}C_{u}O_{2}
Calcd C 69.15 H 5.76 N 14.23%.
Found C 68.95 H 5.61 N 14.19%.

Benzilsemicarbazone, (L⁶).

A similar procedure to the one described for L⁴ was used with L³. A brown pale powdery precipitate was isolated, m.p. 230 °C.

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

Preparation of the complexes

[C₃₄H₃₂N₈Cu₂O₅S₂]
Calcd C 52.59 H 4.12 N 14.73%.
Found C 52.87 H 4.08 N 14.44%.

A_Mₜ 30.22 ohm⁻¹ cm² mol⁻¹. \( \lambda_{\text{max}} \text{ nm (DMF)} 
355, 655 and 850. This complex was also obtained at room temperature using a CHCl₃-EtOH solution of L¹ and an EtOH solution of copper salt. 

[C₃₂H₃₂N₈CuO₄S₂]
To a boiling ethanol solution of L¹ (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.

A_Mₜ 14.50 ohm⁻¹ cm² mol⁻¹. \( \lambda_{\text{max}} \text{ nm (DMF)} 
320, 370 and 840.

A_Mₜ 71.82 ohm⁻¹ cm² mol⁻¹. \( \lambda_{\text{max}} \text{ nm (DMF)} 
310, 470 and 850.
$A_m$, 10.93 ohm$^{-1}$ cm$^2$ mol$^{-1}$. $\lambda_{\text{max}}$/nm (DMF) 270, 425, 480 (sh) and 850.

[3,4,10,11-Tetraphenyl-1,2,5,6,8,9,12,13-octaaza-cyclooctadeca-7,14-dione-2,4,9,11-tetraenide]-
copper(II)-nitrate-ethanol (11)

[(L$^3$)$\text{Cu}^2+$](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$_9$Cu$_6$O$_6$  
Calcd C 54.93 H 4.15 N 18.02%,  
Found C 55.11 H 4.05 N 17.83%.

$A_m$, 69.73 ohm$^{-1}$ cm$^2$ mol$^{-1}$. 

[3,4,10,11-Tetraphenyl-1,2,5,6,8,9,12,13-octaaza-cyclooctadeca-7,14-dithione-2,4,9,11-tetraenide]-
copper(II) ethanol-hydrate (12)

[(L')$_2$ Cu$_2^+$](EtOH)(H$_2$O).

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$_9$CuO$_2$S$_2$  
Calcd C 55.95 H 4.37 N 16.32%,  
Found C 56.23 H 4.27 N 15.89%.

$A_m$, 1.5 ohm$^{-1}$ cm$^2$ mol$^{-1}$. $\lambda_{\text{max}}$/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$_{12}$N$_6$Cu$_2$S$_2$  
Calcd C 45.98 H 3.35 N 20.11%,  
Found C 45.87 H 3.39 N 19.87%.

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

(Bis(benzilbisthiosemicarbazone)dicopper(II))$$_2$$[Cu(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$_9$CuO$_4$S$_4$  
Calcd C 42.88 H 3.13 N 18.76%,  
Found C 43.09 H 3.05 N 18.60%.

$A_m$, 15.5 ohm$^{-1}$ cm$^2$ mol$^{-1}$. $\lambda_{\text{max}}$/nm (DMF) 313, 500 and 550 (sh).

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 polarization 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 C₁₇H₁₇N₃O₂.

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<td>c [Å]</td>
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<td>F(000)</td>
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<tr>
<td>d(calcd), g cm⁻³</td>
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<tr>
<td>µ [cm⁻¹]</td>
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<tr>
<td>Cryst size [mm]</td>
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<tr>
<td>Diffractometer</td>
<td>Enraf-Nonius CAD4</td>
</tr>
<tr>
<td>Radiation</td>
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<tr>
<td>MoKα (λ = 0.71069 Å)</td>
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<tr>
<td>Scan technique</td>
<td>Ω/2θ</td>
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<tr>
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<tr>
<td>rlfns collected</td>
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<td>Unique data (I)≥2σ(I)</td>
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<tr>
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<td>3 rlfns</td>
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<td>R [%]</td>
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<tr>
<td>R1 [%]</td>
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<tr>
<td>Average shift/error</td>
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Results and Discussion

Stable N, O and S-donor Schiff base macrocycle ligands (L₁, L₂ and L₃) 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 (L₄ and L₆) and the mesocyclic L₅. The microcrystalline compounds had elemental analyses consistent with the formulation given. White crystals of L₅ were grown by slow evaporation of an EtOH solution.

Figure 1 shows an ORTEP¹⁵ view of the two independent, but similar molecules with their intermolecular hydrogen bonds between N₅'···O₁ and N₅···O₁', with distances of 2.876(5) and 2.825(5) Å, respectively, and another intermolecular interaction between O₁···N₃(3.01,1.73,2.22) and O₁'···N₃(3.01,1.73,2.22), 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 N₃ and 0.15 Å for N₅'. 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 inserted in the lattice. Table III summarizes important bond lengths and angles.

As shown in the Figure an ethanolate group is bonded to the C₆ atom of the new heterocycle formed in the reaction. This results may be explained in terms of an EtOH addition across one

Table II. Fractional atomic coordinates and equivalent isotropic displacement parameters for C₁₇H₁₇N₃O₂.

<table>
<thead>
<tr>
<th>Atom</th>
<th>x/a</th>
<th>y/b</th>
<th>z/c</th>
<th>U eq</th>
</tr>
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<td>0.9906(2)</td>
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<td>0.1811(3)</td>
<td>1.2875(3)</td>
<td>63(2)</td>
</tr>
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*Table II. Fractional atomic coordinates and equivalent isotropic displacement parameters for C₁₇H₁₇N₃O₂.*

*U eq = 1/3 Σ Uᵢ,j aᵢ* aᵢ' aⱼ* aⱼ' 10⁻⁶.*
of the azomethine linkages formed in a previous step, with a simultaneous elimination of a water molecule.

The $^1$H and $^{13}$C NMR data of the ligands obtained in CDCl$_3$ and/or (CD$_3$)$_2$SO solution are given in Table IV and V.

The $^1$H 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 moiety. The spectra of L$^2$ and L$^5$ show chemical shifts in the range 86–88 ppm, consistent

<table>
<thead>
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<th>Bond Lengths (Å)</th>
<th>Angles (°)</th>
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Table III. Selected bond lengths (Å) and angles (°) for C$_{17}$H$_{17}$N$_2$O$_2$. Fig. 1. ORTEP view of C$_{17}$H$_{17}$N$_2$O$_2$ (Ligand L$^3$).
with saturation of the imino groups as resulting from EtOH insertion.

In the mass spectra of L⁴ and L⁶ 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%) C₆H₅- CO- of L⁶ 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 L⁵ complex, 16, are non-electrolytes, but 9 and 11 are 1:1 electrolytes owing to partial liberation of HNO₃.

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 L² and L⁴ complexes (8, 13,
Table VI. Selected IR bands (cm⁻¹) of the ligands and copper(II) complexes.

<table>
<thead>
<tr>
<th></th>
<th>v(NH)⁻⁺</th>
<th>v(C=N)⁻⁺</th>
<th>v(C=O) (Benzil)</th>
<th>δ(NH₂)⁻⁻</th>
<th>v(C=N)⁻⁻</th>
<th>Amide I or Thioamide I</th>
<th>Thioamide IV</th>
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<td>3323</td>
<td>-</td>
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<td>-</td>
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<td>L²</td>
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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 L¹ and L³ complexes (7, 9, 10, 11 and 12) agree with copper nitrogen interaction, which is confirmed for the L¹ complexes (7, 9 and 12) by the new band assigned to v (C=N=N)⁻⁻ vibration of the "enyl" form¹⁹ of the ligand. The IR bands attributable to the NO₃⁻ 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) complexes²⁰. 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 PB90–0227–C02–01).
     b) H. G. Petering, H. H. Buskirk, J. A. Crim, G. J. Giessen, Pharmacologist 5, 271 (1963);
     (1980).