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FORMACIÓN DE COMPLEJO OLIGONUCLEAR CON EL LIGANDO BIS-BIDENT ADO N',N', N'''', N'''-TETRAETILO -N,N'-PIRIDINA-2,6-DICARBONILO-BIS(TIOUREA) EN DISOLUCIÓN


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FORMACIÓN DE COMPLEJO OLIGONUCLEAR CON EL LIGANDO BIS-BIDENTADO N',N',N''',N''''-TETRAETILO-Ν,Ν''-PIRIDINA-2,6-DICARBONOLO-BIS(TIOUREA) EN DISOLUCIÓN

Lothar Beyer *, Frank Dietze, Uwe Schröder, Lutz Quas Luis M. N. B. F. Santos and Bernd Schröder **

RESUMEN

El ligando N',N',N''',N''''-tetraetil-N,N''-piridina-2,6-dicarbonilo-bis(tiourea), H_[tepytu], 2H_L, reacciona con níquel(II) formando un complejo neutro binuclear del tipo Ni_L_2. La existencia del complejo con esta constitución fue encontrado en una mezcla 75%v/v 1,4-dioxano/agua.

La optimización geométrica en fase gaseosa ha sido ejecutada por un cálculo ab-initio nivel B3LYP/SDD. El cálculo mostró que el rígido piridín-centrado complejo dinuclear forma una cavidad central bastante grande para permitir una interacción intermolecular.

Palabras Clave: Complejos oligonucleares; constantes de estabilidad, dioxano/agua; níquel, ligandos, tiourea.

OLIGONUCLEAR COMPLEX FORMATION OF THE BIS-BIDENTATE LIGAND N',N',N''',N''''-TETRAETHYL-N,N''-PYRIDINE-2,6-DICARBONYL-BIS(THIOUREA) IN SOLUTION

ABSTRACT

With nickel(II), the potential ligand N',N',N''',N''''-tetraethyl-N,N''-pyridine-2,6-dicarbonyl-bis(thiourea), H_2[tepytu], forms a neutral binuclear complex of the type Ni_2L_2. The occurrence of a complex of this constitution was found in a 75%v/v 1,4-dioxane/water mixture.

A geometry optimization in the gas phase was performed by ab-initio calculations at the B3LYP/SDD level of theory. It shows that the rigid pyridine-centered binuclear complex forms a central cavity in-between the pyridine, large enough to allow intermolecular interaction.
Key words: Oligonuclear complexes; stability constants; dioxane/water, nickel; thiourea ligand

INTRODUCTION

Publications on stability constants of oligonuclear complexes are scarce. Bis-bidentate chalcogenourea ligands are generally able to form oligo- or polymeric complexes of many different structures, depending on the molecular shape of the ligand, the nature of the bridging group, the sequence of the donor atoms, as well as on the nature of the metal ion.

Only recently, as part of a broad study on the thermochemistry of transition metal complexes of bidentate chalcogenourea ligands and analogues, the measurement of thermochemical properties of representatives of bis-bidentate chalcogenourea ligand systems gained momentum.

Despite of a considerable number of different bi- or tri-nuclear metal complexes of bis-bidentate acylchalcogenourea-type ligands synthesized in solid state in the past, we are not aware of any publication on their thermodynamic stability in solution. Amazingly enough, the same applies to the thoroughly studied complexes of â-tri- and â-tetraketones, with the unique exception of.

This situation may be in part due to the fact that oligonuclear complexes well characterized in their respective solid states are often only slightly soluble and can undergo a change of their composition and molecular weight in protic solution.

Ligands with similar structural motifs like in the title compound H₄[tepytu] have been the target of investigation on their coordination chemistry. Of special interest is their potential ability to build up metalla-(pseudo)-crown ethers with a selective incorporation of ions or molecules in the resulting cavities (metal-organized host). A geometry optimization in gas phase, by ab-initio calculations at the B3LYP/SDD level of theory, should yield information concerning the cavity size (figura 1).

Figure 1. The title ligand N,N,N”,N”-tetraethyl-N,N”-pyridine-2,6-dicarbonyl-bis(thiourea) H₄[tepytu] (H₄L)
**EXPERIMENTAL**

*Synthesis and characterization of the nickel(II) complex [Ni$_2$L$_2$(H$_2$O)$_2$(CH$_3$OH)$_2$]*

To a solution of 0.249 g (1 mmol) nickel(II) acetate tetrahydrate in 30 ml methanol, 0.395 g H$_3$[tepytu] $^{11}$, dissolved in 30 ml methanol, were added dropwise. The mixture was left stirring for three hours. Than, the volume of the solution was reduced to 15 ml, and 15 ml of H$_2$O were added slowly. The nickel(II) complex crystallized overnight as fine green needles which were filtrated and air-dried. Yield: 0.832 g (80%), mp 203-206 Celsius (dec.)

C$_{36}$H$_{62}$Ni$_2$O$_{10}$S$_4$ (1040.56 g/mol): calc.: C 41.55; H 6.01; N 13.46; Ni 11.28; O 15.37; S 12.32 %; found: C 40.29; H 5.88; N 13.45; Ni 10.95; O 15.60; S 11.34 %.

FAB-MS (matrix: 3-nitrobenzyl alcohol): $m/z$ (fragment ion, rel. int. in %) 1037
(([Ni$_2$L$_2$(H$_2$O)$_2$](CH$_3$OH)$_2$)-3H), 30), 962 (([Ni$_2$L$_2$(H$_2$O)$_2$]-4H), 58), 904 (([Ni$_2$L$_2$]), 45), 832 (([Ni$_2$L$_2$]-NET$_3$), 100), 452 ([NiL$^+$], 30), 420 (([NiL$^+$]-S), 8)

IR (KBr) $\tilde{\nu}$ [cm$^{-1}$] 3430s (br), 2473m, 1559s, 1429m, 1377s, 1253m


\[ \text{i}_{\text{eff}} = 3.23 \text{ B.M. per Ni (at } T = 298 \text{ K)} \]

**Potentiometric measurements**

All measurements were carried out under an argon atmosphere in a 1,4-dioxane/water mixture {75% v/v, $T = 298.15 \text{ K}$, ionic strength = 0.1 mol/l ([(CH$_3$)$_2$N][NO$_3$]) using an automated titration equipment (PHM 84, ABU 80, RADIOMETER COPENHAGEN) driven by an IBM compatible PC. As a cell, a combination of G202B/K701 electrodes (RADIOMETER COPENHAGEN) was used. The cell was calibrated in the $-\lg[H^+]$ scale ($pK_{\text{HBR}} = 16.74$) by strong acid/base (carbonate free KOH) titration. The potentiometric data were processed with MINIQUAD 75A/B as well as HYPERQUAD.

During the pH potentiometric study in a 75%v/v 1,4-dioxane/water mixture, the concentrations of the reacting species and the ratio of their concentrations were varied within a wide range, between the limits of solubility and measurability (table 1).

**Table 1.** Concentrations of nickel(II) and ratio of concentrations used in the search for the preferred coordination models with the title ligand $N,N',N''',N'''$-tetraethyl-$N,N''$-pyridine-2,6-dicarbonyl-bis(thiourea) H$_3$[tepytu] (in a 75%v/v 1,4-dioxane/water mixture.).

<table>
<thead>
<tr>
<th>[H$_3$L] : [Ni(II)]</th>
<th>[Ni(II)]/ mol·l$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.6:1</td>
<td>2.5 x $10^{-3}$</td>
</tr>
<tr>
<td>0.8:1</td>
<td>1 x $10^{-3}$</td>
</tr>
<tr>
<td>1:1</td>
<td>1 x $10^{-3}$, 5 x $10^{-3}$</td>
</tr>
<tr>
<td>2:1</td>
<td>5.2 x $10^{-4}$, 1 x $10^{-3}$, 2.45 x $10^{-3}$</td>
</tr>
<tr>
<td>4:1</td>
<td>5.2 x $10^{-4}$</td>
</tr>
<tr>
<td>6:1</td>
<td>1 x $10^{-3}$</td>
</tr>
<tr>
<td>34:1</td>
<td>5.2 x $10^{-4}$</td>
</tr>
</tbody>
</table>
In order to derive reliable stability constants by the chosen method, a preliminary step was carried out. Potentiometric titrations with the simple bidentate ligand $N,N$-diethyl-$N'$-benzoylthiourea (DEBTU) $^{12}$ and nickel(II) from a two-fold up to a 50-fold ligand concentration were performed.

**Computational details**

All calculations have been performed using the density functional theory (DFT) $^{13}$. DFT calculations were performed with the hybrid B3LYP exchange correlations functional $^{14-16}$. A full geometry optimization of the binuclear complex has been carried out with the SDD basis set (D95V $^{17}$ basis set up to sulphur and the Stuttgart/Dresden core potentials $^{18}$ for nickel). At the same theoretical level, analytical frequency calculations were performed to ensure real minima ($N_{eq}=0$). All the theoretical calculation were performed using the Gaussian-03 program $^{19}$.

**RESULTS AND DISCUSSION**

The ligand H$_2$[tepytu] and nickel(II) yield a bimetalla cycle Ni$_2$L$_2$ which could be isolated in solid state.

Table 2 shows the very small scattering of the constant of the related mononuclear nickel(II) complex NiL' in the preliminary tests. In spite of the increasing ligand concentration, an unchanged model of coordination is indicated.

<table>
<thead>
<tr>
<th>$[HL] : [Ni(II)]$</th>
<th>$lg\beta_2$ (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2:1</td>
<td>15.11 (0.01)</td>
</tr>
<tr>
<td>4:1</td>
<td>15.28 (0.004)</td>
</tr>
<tr>
<td>8:1</td>
<td>15.20 (0.008)</td>
</tr>
<tr>
<td>25:1</td>
<td>15.19 (0.01)</td>
</tr>
<tr>
<td>50:1</td>
<td>15.15 (0.02)</td>
</tr>
</tbody>
</table>

The program MINIQUAD A/B75$^{21}$ differs slightly from its further development HYPERQUAD$^{22}$ in its respective strategy of minimization. Therefore, the implemented statistical treatments of the results of each program differ, as well. We used the following criteria of the program for evaluation of the computational output $^{23-25}$: In MINIQUAD, we consider $\delta$ (standard deviation of the sample) as well as $R$ (a measure of the agreement between experimental and calculated data, calculated by a Hamilton test $^{26}$). $\delta$ and $R$ should be minimal ($R < 0.004$) to correspond to an acceptable model selection.
The calculations have been repeated with the HYPERQUAD suite of programs, which applies improved minimization routines to directly measured quantities, with optionally weighted experimental errors. In HYPERQUAD, we consider $\sigma$ (standard deviation of the sample) as well as sigma (scaled sum of squares).

Each model calculation starts with an estimate of the formation constant. In case of a successful calculation, the refined formation constant, errors, correlation coefficients, including probability distributions, are summarized in the output.

If the model for the respective complex formation is ill-defined, it will be rejected. A proper model selection is especially problematic in systems in which it is unclear, what chemical species will appear in considerable concentrations in the reaction solution.

Both programs give nearly the same numerical results. All stability constants of Ni$_2$L$_2$ fall into the range from $\log\beta = 32.10$ to $\log\beta = 32.68$ (tables 3-4).

**Table 3.** Typical stability constants of the dinuclear nickel(II) complex as a function of the concentration of the bis-bidentate ligand $N',N'',N'''-tetraethyl-N,N''$-pyridine-2,6-dicarbonyl-bis(thiourea) $H_2[tepytu]$ (H,L) vs. [Ni(II)] in a 75% v/v 1,4-dioxane/water mixture {75% v/v, $T = 298.15$ K, ionic strength = 0.1 mol/l ([(CH$_3$)$_3$N]NO$_3$)} (MINIQUAD 75). The acidity constants of the ligand accounts for $pK_{S1} = 10.26$ and $pK_{S2} = 11.55$ [this work].

<table>
<thead>
<tr>
<th>$[H_2L]:[Ni(II)]$</th>
<th>$\log K (\sigma)$</th>
<th>$R$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1</td>
<td>32.10 (0,01)</td>
<td>0.008643</td>
</tr>
<tr>
<td>2:1</td>
<td>32.18 (0,007)</td>
<td>0.001945</td>
</tr>
<tr>
<td>4:1</td>
<td>32.42 (0.016)</td>
<td>0.001933</td>
</tr>
<tr>
<td>6:1</td>
<td>32.68 (0,01)</td>
<td>0.001131</td>
</tr>
</tbody>
</table>

**Table 4.** Typical stability constants of the dinuclear nickel(II) complex as a function of the concentration of the bis-bidentate ligand $N',N'',N'''-tetraethyl-N,N''$-pyridine-2,6-dicarbonyl-bis(thiourea) $H_2[tepytu]$ (H,L) vs. [Ni(II)] in a 75% v/v 1,4-dioxane/water mixture {75% v/v, $T = 298.15$ K, ionic strength = 0.1 mol/l ([(CH$_3$)$_3$N]NO$_3$)} (HYPERQUAD). The acidity constants of the ligand accounts for $pK_{S1} = 10.26$ and $pK_{S2} = 11.55$ [this work].

<table>
<thead>
<tr>
<th>$[H_2L]:[Ni(II)]$</th>
<th>$\log K (\sigma)$</th>
<th>Sigma</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1</td>
<td>32.30 (0,015)</td>
<td>3.2860</td>
</tr>
<tr>
<td>2:1</td>
<td>32.31 (0,008)</td>
<td>0.9409</td>
</tr>
<tr>
<td>4:1</td>
<td>32.57 (0.014)</td>
<td>1.9944</td>
</tr>
<tr>
<td>6:1</td>
<td>32.58 (0,01)</td>
<td>3.8734</td>
</tr>
</tbody>
</table>
For the molar ratios \([H_2L] : [Ni^{II}]\) of 1:1, 2:1, 4:1 and 6:1 (with the respective \(Ni^{II}\) – concentration falling in the range \(5 \times 10^{-4} – 2.4 \times 10^{-3}\) mol x l\(^{-1}\)), MINIQUAD 75 preferred the model of the binuclear \([Ni_2L_2]\) complex formation. These values have been in accordance with the respective results of the HYPERQUAD calculations.

The results show a consequent preference of the \([Ni_2L_2]\) model, found in the range of usual concentration ratios in potentiometric titrations. These findings are satisfactory in a coordination chemistry sense, since the formation of a dimetalla macrocycle with a square-planar S,O-coordination is anticipated. Nevertheless, in the case of more extreme concentration ratios, like \([H_2L] : [Ni^{II}]\) being 34:1 or 0.6:1, the monomer was the encountered prevailing chemical specie in the course of potentiometric titration.

There is a further interesting feature of the coordinated rigid pyridine-centered \(Ni\{tepytu\}\) which can in part answer the remaining question about the verified existence of the dimeric complex in solution. Since the previously obtained crystals of the nickel(II) complex had not yet been suitable for X-ray structural determination, a geometry optimization for the gas phase was performed, as described in the Computational details section. The complex exhibits a saddle-like shape. The pyridine rings are twisted, thus allowing for the planarity of the nickel coordination sphere, which maintains a square planar geometry (figures 2 and 3).

**Figure 2.** The structure of the nickel(II) complex \([Ni_2L_2(H_2O)_2]\), formed of \(H_2\{tepytu\}\) \((H_2L)\), in the gas phase, obtained by a geometry optimization. DFT calculations were performed with the hybrid B3LYP exchange correlations functional. The full geometry optimization of the binuclear complex has been carried out with the SDD basis set. The complex shows an overall symmetry of \(C_{2v}\).
The result shows the intramolecular distances in the cavity of the complex. This cavity can include guest molecules like water or methanol as realized, depending on the solvent. It can also incorporate cations like sodium. The guest may stabilize the chelate in contrast to a structural related ligand without the pyridine nitrogen.

Further X-ray structural determination work is under way.

ACKNOWLEDGEMENTS

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LITERATURE


