

*Dedicado con motivo del 75 aniversario de la fundación de la
Sociedad Química del Perú*

FORMACIÓN DE COMPLEJO OLIGONUCLEAR CON EL LIGANDO BIS-BIDENTADO N',N',N'',N''' -TETRAETILO- N,N'' - PIRIDINA-2,6-DICARBONILO-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), $H_2[tepytu]$, H_2L , reacciona con níquel(II) formando un complejo neutro binuclear del tipo Ni_2L_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), $H_2[tepytu]$, H_2L , 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.

* Institut für Anorganische Chemie, Universität Leipzig, Johannisallee 29, D-04103 Leipzig, Germany. e-mail: beyinorg@chemie.uni-leipzig.de

** Centro de Investigação em Química, Departamento de Química, Faculdade de Ciências, Universidade do Porto, Rua do Campo Alegre, 687, P-4169-007 Porto, Portugal
e-mail: bschrode@fc.up.pt

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 ligands¹ and analogues²⁻⁴, the measurement of thermochemical properties of representatives of bis-bidentate chalcogenourea ligand systems gained momentum⁵.

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 past⁶⁻⁸, we are not aware of any publication on their thermodynamic stability in solution. Amazingly enough, the same applies to the thoroughly studied complexes of β -tri- and β -tetraketones, with the unique exception of⁹.

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 $H_2[tepytu]$ 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)¹⁰. A geometry optimization in gas phase, by ab-initio calculations at the B3LYP/SDD level of theory, should yield information concerning the cavity size (figure 1).

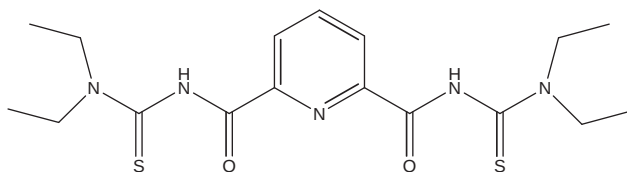


Figure 1. The title ligand N',N',N'',N''' -tetraethyl- N,N'' -pyridine-2,6-dicarbonyl-bis(thiourea) $H_2[tepytu]$ (H_2L)

EXPERIMENTAL

Synthesis and characterization of the nickel(II) complex $[Ni_2L_2(H_2O)_4](CH_3OH)_2$

To a solution of 0,249 g (1mmol) nickel(II)acetate tetra-hydrate in 30ml methanol, 0,395 g $H_2[tepytu]$ ¹¹, dissolved in 30ml methanol, were added dropwise. The mixture was left stirring for three hours. Then, the volume of the solution was reduced to 15 ml, and 15 ml of H_2O 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.)

$C_{36}H_{62}N_{10}Ni_2O_{10}S_4$ (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

$([Ni_2L_2(H_2O)_4](CH_3OH)_2 \cdot 3H_2O)$, 962 $([Ni_2L_2(H_2O)_4] \cdot 4H_2O)$, 58, 904 $([Ni_2L_2]^{+})$, 45,

832 $([Ni_2L_2] \cdot NEt_3)^{+}$, 100, 452 $([NiL]^{+})$, 30, 420 $([NiL] - S)^{+}$, 8)

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

$\chi_{eff} = 3,23$ B.M.per Ni (at $T = 298$ K)

Potentiometric measurements

All measurements were carried out under an argon atmosphere in a 1,4-dioxane/water mixture {75% v/v, $T = 298,15$ K, ionic strength = 0,1 mol/l $([(CH_3)_4N]NO_3)$ } 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 ($pK_{H_2O} = 16,74$) by strong acid/base (carbonate free KOH) titration. The potentiometric data were processed with MINQUAD 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) $H_2[tepytu]$ (in a 75%v/v 1,4-dioxane/water mixture.).

$[H_2L] : [Ni(II)]$	$[Ni(II)]/ mol \cdot l^{-1}$
0,6:1	$2,5 \times 10^{-3}$
0,8:1	1×10^{-3}
1:1	$1 \times 10^{-3}, 5 \times 10^{-3}$
2:1	$5,2 \times 10^{-4}, 1 \times 10^{-3}, 2,45 \times 10^{-3}$
4:1	$5,2 \times 10^{-4}$
6:1	1×10^{-3}
34:1	$5,2 \times 10^{-4}$

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 functional¹⁴⁻¹⁶. A full geometry optimization of the binuclear complex has been carried out with the SDD basis set (D95V¹⁷ basis set up to sulphur and the Stuttgart/Dresden core potentials¹⁸ for nickel). At the same theoretical level, analytical frequency calculations were performed to ensure real minima ($N_{\text{img}}=0$). All the theoretical calculation were performed using the Gaussian-03 program¹⁹.

RESULTS AND DISCUSSION

The ligand $\text{H}_2[\text{tepytu}]$ and nickel(II) yield a bimetalla cycle Ni_2L_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'_2 in the preliminary tests. In spite of the increasing ligand concentration, an unchanged model of coordination is indicated.

Table 2. Stability constant of the mononuclear nickel(II) complex as a function of the concentration of the bidentate ligand *N,N*-diethyl-*N'*-benzoylthiourea (DEBTU, HL'), $[\text{Ni(II)}] = 5,18 \times 10^{-4} \text{ mol l}^{-1}$ in a 75%v/v 1,4-dioxane/water mixture {75% v/v, $T = 298,15 \text{ K}$, ionic strength = 0,1 mol/l $[(\text{CH}_3)_4\text{N}]\text{NO}_3$ }. The acidity constant of the ligand accounts for $\text{pK} = 10,87$ ²⁰.

[HL] : [Ni(II)]	$\lg K_2$ (s)
2:1	15,11 (0.01)
4:1	15,28 (0.004)
8:1	15,20 (0.008)
25:1	15,19 (0.01)
50:1	15,15 (0.02)

The program MINIQUAD A/B75²¹ differs slightly from its further development HYPERQUAD²² 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 output²³⁻²⁵: In MINIQUAD, we consider σ (standard deviation of the sample) as well as R (a measure of the agreement between experimental and calculated data, calculated by a Hamilton test²⁶). σ and R should be minimal ($R < 0,004$) to correspond to an acceptable model selection.²⁷⁻²⁹

The calculations have been repeated with the HYPERQUAD suite of programs³⁰, which applies improved minimization routines to directly measured quantities, with optionally weighted experimental errors. In HYPERQUAD, we consider δ (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_2L_2 fall into the range from $\lg K = 32,10$ to $\lg K = 32,68$ (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''',N'''' -tetraethyl- N,N' -pyridine-2,6-dicarbonyl-bis(thiourea) $H_2[tepytu]$ (H_2L) 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 ($[(CH_3)_4N]NO_3$)} (MINIQUAD 75). The acidity constants of the ligand accounts for $pK_{s1} = 10,26$ and $pK_{s2} = 11,55$ [this work].

$[H_2L] : [Ni(II)]$	$\lg K (\delta)$	R
1:1	32,10 (0,01)	0,008643
2:1	32,18 (0,007)	0,001945
4:1	32,42 (0,016)	0,001933
6:1	32,68 (0,01)	0,001131

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''',N'''' -tetraethyl- N,N' -pyridine-2,6-dicarbonyl-bis(thiourea) $H_2[tepytu]$ (H_2L) 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 ($[(CH_3)_4N]NO_3$)} (HYPERQUAD). The acidity constants of the ligand accounts for $pK_{s1} = 10,26$ and $pK_{s2} = 11,55$ [this work].

$[H_2L] : [Ni(II)]$	$\lg K (\delta)$	Sigma
1:1	32,30 (0,015)	3,2860
2:1	32,31 (0,008)	0,9409
4:1	32,57 (0,014)	1,9944
6:1	32,58 (0,01)	3,8734

For the molar ratios $[\text{H}_2\text{L}] : [\text{Ni}^{\text{II}}]$ of 1:1, 2:1, 4:1 and 6:1 (with the respective Ni^{II} – concentration falling in the range $5 \times 10^{-4} - 2,4 \times 10^{-3} \text{ mol} \times \text{l}^{-1}$), MINQUAD 75 preferred the model of the binuclear $[\text{Ni}_2\text{L}_2]$ complex formation. These values have been in accordance with the respective results of the HYPERQUAD calculations.

The results show a consequent preference of the $[\text{Ni}_2\text{L}_2]$ 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 $[\text{H}_2\text{L}] : [\text{Ni}^{\text{II}}]$ 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 $\text{Ni}[\text{tepytu}]$ 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).

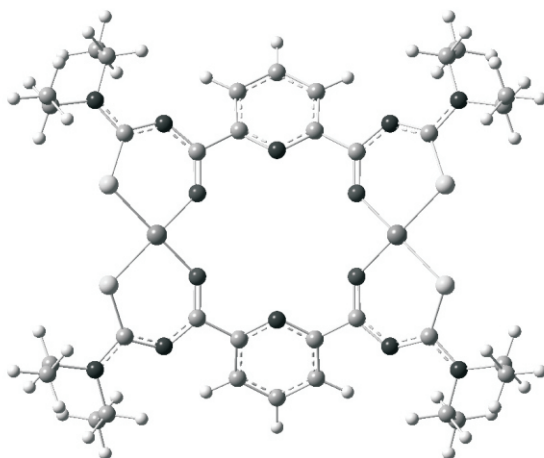


Figure 2. The structure of the nickel(II) complex $[\text{Ni}_2\text{L}_2(\text{H}_2\text{O})_4]$, formed of $\text{H}_2[\text{tepytu}]$ (H_2L), in the gas phase, obtained by a geometry optimization. DFT calculations were performed with the hybrid B3LYP exchange correlations functional. The full geometry optimization of the binuclear complex has been carried out with the SDD basis set. The complex shows an overall symmetry of C_{2v} .

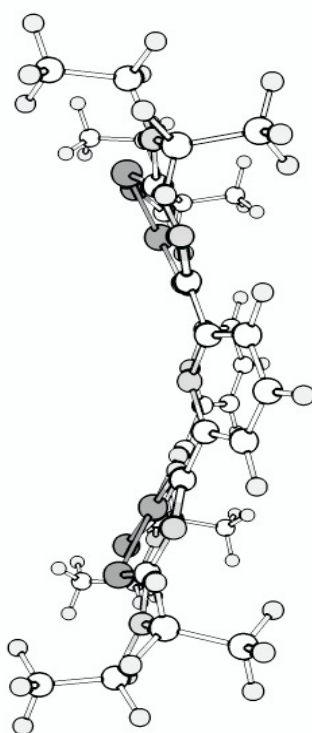


Figure 3. Side view of the structure of Ni[tepytu] in the gas phase, obtained by the same geometry optimization

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

The authors thank Sylke Schmidt (from Universität Leipzig) for some potentiometric measurements. Bernd Schröder is grateful to Fundação Para a Ciência e Tecnologia, Lisboa, Portugal, and the European Social Fund (ESF) under the 3rd Community Support Framework (CSF), for the award of a Post-Doc scholarship (PRAXIS XXI/ BPD 35131/2000).

LITERATURE

1. Ribeiro da Silva, M. A. V.; Ribeiro da Silva, M. D. M. C.; Silva, L. C. M.; Gomes, J. R. B.; Damas, A. M.; Dietze, F.; Hoyer, E. *Inorg. Chim. Acta* **2003**, *356*, 95-102.
2. Ribeiro da Silva, M. A. V.; Santos, L. M. N. B. F.; Schröder, B.; Dietze, F.; Beyer, L. *J. Chem. Thermodynamics* **2004**, *36*, 627-631.
3. Ribeiro da Silva, M. A. V.; Santos, L. M. N. B. F.; Schröder, B. *J. Chem. Thermodynamics* **2004**, *36*, 753-757.
4. Ribeiro da Silva, M. A. V.; Santos, L. M. N. B. F.; Schröder, B. *J. Chem. Thermodynamics* **2007**, *39*, 684-688.
5. Ribeiro da Silva, M. A. V.; Santos, L. M. N. B. F.; Schröder, B.; Beyer, L.; Dietze, F. *J. Chem. Thermodynamics* **2007**, *39*, 279-283.
6. Köhler, R.; Kirmse, R.; Richter, R.; Sieler, J.; Hoyer, E.; Beyer, L. *Z. Anorg. Allg. Chem.* **1986**, *537*, 133-144.
7. König, K.-H.; Kuge, M.; Kaul, L.; Pletsch, H.-J. *Chem. Ber.* **1987**, *120*, 1251-1253.
8. Koch, K. R.; Bourne, S. A.; Coetzee, A.; Miller, J. *J. Chem. Soc., Dalton Trans.* **1999**, *18*, 3157-3161.
9. Hynes, M. J.; Walsh, J. *J. Chem. Soc., Dalton Trans.* **1985**, *8*, 1543-1546.
10. Kobake, Y.; Satoh, Y. *J. Am. Chem. Soc.* **1992**, *114*, 789-790.
11. Schröder, U.; Beyer, L.; Sieler, J. *Inorg. Chem. Commun.* **2000**, *3*, 630-633.
12. Beyer, L.; Hoyer, E.; Hennig, H.; Kirmse, R. **1975**, *317*, 829.
13. Koch, W.; Holthausen, M. C. A. *Chemist's Guide to Density Functional Theory*, 2nd ed.; Wiley-VCH: Weinheim, 2002.
14. Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648-5652.
15. Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098-3100.
16. Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785-789.
17. Dunning Jr., T. H.; Hay, P. J. in *Modern Theoretical Chemistry*, Ed. Schaefer, H. F. III, Vol. 3 (Plenum, New York) 1976, 1-28.
18. Dolg, M.; Wedig, U.; Stoll, H.; Preuss, H. *J. Chem. Phys.* **1987**, *86*, 866-872.

19. Gaussian 03, Revision C.02, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A.; Gaussian, Inc., Wallingford CT, 2004.
20. Beyer, L.; Hoyer, E.; Liebscher, J.; Hartmann, H. *Z. Chem.* **1981**, *21*, 81-91.
21. Gans, P.; Sabatini, A.; Vacca, A. *Inorg. Chim. Acta* **1976**, *18*, 237-239.
22. Gans, P.; Sabatini, A.; Vacca, A. *Talanta* **1996**, *43*, 1739-1753.
23. Bologni, L.; Sabatini, A.; Vacca, A. *Inorg. Chim. Acta* **1983**, *69*, 71-75.
24. Gans, P.; Sabatini, A.; Vacca, A. *J. Chem. Soc., Dalton Trans.* **1985**, *6*, 1195-1200.
25. Lomozik, L.; Jaskolski, M.; Wojciechowska, A. *Pol. J. Chem.* **1991**, *65*, 1797-1807.
26. Sabatini, A.; Vacca, A.; Gans, P. *Talanta* **1974**, *21*, 53-77.
27. Vacca, A.; Sabatini, A.; Gristina, M. A. *Coord. Chem. Rev.* **1972**, *8*, 45-53.
28. Sabatini, A.; Vacca, A. *Coord. Chem. Rev.* **1975**, *16*, 161-169.
29. Legett, D. J. (ed.) *Computational Methods for the Determination of Formation Constants*, Plenum Press, New York, 1985.
30. Gans, P.; Sabatini, A.; Vacca, A. *Hyperquad Manual*, Protonic Software (1995).