Inorganica
Chimica Acta
*Preliminary Communication*

# Synthesis and complexation behaviour of a double-armed crown thioether ligand

Francesco Neve* and Mauro Ghedini
*Dipartimento di Chimica, Università della Calabria, I-87030 Arcavacata di Rende (CS) (Italy)*

(Received October 25, 1993)

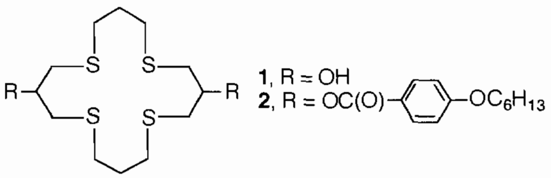
## Abstract

The novel macrocycle 3,11-bis[4-(n-hexyloxy)benzoyloxy]-1,5,9,13-tetrathiacyclohexadecane (**2**) was obtained as a mixture of *cis* and *trans* isomers by reaction of 1,5,9,13-tetrathiacyclohexadecane-3,11-diol (**1**) (*cis* and *trans*) and 4-(n-hexyloxy)benzoyl chloride. Ligand **2** readily reacts with $[Cu^I(MeCN)_4]PF_6$ to afford the white, cationic complex $[Cu^I(\mathbf{2})]PF_6$, wherein **2** acts as a tetradentate donor. Polarising microscopy showed no mesomorphism of either **2** or the $[Cu^I(\mathbf{2})]PF_6$ species.

*Key words:* Copper complexes; Crown thioether complexes

Ligand design is always a crucial step in coordination chemistry studies as the nature and architectural organisation of the donors will strongly influence the chemical and physical properties of the complexed species. This is especially true in the area of metallomesogens (metal-containing liquid crystals) wherein the structure–properties relationship is well established [1], although one must better refer to the molecular shape rather than to the coordination geometry.

In our quest for macrocyclic thermotropic metallomesogens [2], we planned to properly modify simple polydentate macrocycles in order to get ligands with a predetermined shape. The introduction of a given number of substituents onto a macrocycle does not necessarily change the coordination character of the ligand, although it can result in a dramatic change of the supramolecular organisation [3]. Thus grafting two *p*-alkoxybenzoyl chains to a diaza tetrathia 18-membered macrocycle led to a non-mesogenic ligand which eventually afforded a Pd(II) complex with mesomorphic behaviour [2].



The macrocycle $[16]aneS_4$-diol (Aldrich, mixture of *cis* and *trans*) (**1**) was reacted with 2.5 equiv. of 4-(n-hexyloxy)benzoyl chloride in the presence of 2.5 equiv. of $NEt_3$ under reflux conditions (benzene, 20 h). After workup the novel 3,11-bis[4-(n-hexyloxy)benzoyloxy]-1,5,9,13-tetrathiacyclohexadecane (**2**)** was obtained as a white solid in 20% yield. Macrocycle **2**, which has an ideal elongated shape, is actually a mixture of *cis* and *trans* isomers as can be easily ascertained by $^{13}C\{^1H\}$ NMR spectroscopy (Fig. 1).

Monomeric macrocyclic complexes incorporating 16-membered tetrathia ligands are scarce [4, 5] and most of them adopt an octahedral geometry with the macrocycle occupying all the equatorial positions. Ligands such as $[16]aneS_4$ can also accommodate tetrahedral coordination environments as predicted for $[Cu^I([16]aneS_4)]^+$ [6].

The reaction of one equivalent of **2** with one equivalent of $[Cu^I(MeCN)_4]PF_6$ in $CH_2Cl_2$/MeCN followed by n-hexane addition gave the cationic $[Cu^I(\mathbf{2})]PF_6$† as a white solid in 62% yield. Spectroscopic characterisation is fully consistent with the monomeric formulation, although the presence of the different isomers is not so obvious from room temperature NMR spectra. In particular, the $^{13}C$ NMR spectrum of the complex (Fig. 1, upper trace) shows four distinct resonances for the carbon atoms of the macrocyclic core as expected for a ligand tetracoordinated in a symmetrical fashion.

Polarising optical microscopy showed that, despite our expectations, both **2** and its copper(I) derivative

---

*Author to whom correspondence should be addressed.

**Satisfactory elemental analysis results. FT-IR (Nujol mull): $\nu$ (C=O) 1708 $cm^{-1}$. $^1H$ NMR ($CDCl_3$, 300 MHz): $\delta$ 0.91 (t, 6H), 1.33–1.46 (m, 12H), 1.79 (m, 4H), 2.01 (m, 4H, $H_d$), 2.70–3.08 (m, 16H, $H_c+H_b$), 4.00 (t, 6H), 5.29 (m, 2H, $H_a$), 6.90 (d, 4H), 7.99 (d, 4H). $^{13}C\{^1H\}$ NMR ($CDCl_4$, 75.5 MHz): $\delta$ 13.92, 22.52, 25.62, 29.07, 29.61, 29.92, 31.48, 31.51, 31.62, 34.95, 35 14, 68.30, 72.46, 72 86, 114.22, 122.18, 131.78, 163.24, 165.72, 165.78.

†FT-IR (Nujol mull): $\nu$ (C=O) 1712(br) $cm^{-1}$. $\Lambda_M$ ($9\times10^{-4}$ M, $MeNO_2$): 63.4 $\Omega^{-1}\,M^{-1}\,cm^2$. FAB mass spectrum (3-nitrobenzyl alcohol matrix): *m/z* 799 ($[^{63}Cu(\mathbf{2})]^+$). $^1H$ NMR ($CDCl_3$, 300 MHz): $\delta$ 0.90 (t, 6H), 1.33–1.48 (m, 12H), 1.79 (m, 4H), 2.17 (m, 4H, $H_d$), 3.03 (m, 8H, $H_b$ or $H_c$), 3.27 (m, 8H, $H_c$ or $H_b$), 4.00 (t, 6H), 5.47 (m, 2H, $H_a$), 6.93 (d, 4H), 7.95 (d, 4H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.5 MHz): $\delta$ 13.90, 22.51, 24.25, 25.61, 29.04, 31.50, 35.27, 38.04, 68.47, 114.55, 120.93, 131.94, 163.86, 164.93.

*SSDI* 0020-1693(93)03775-6

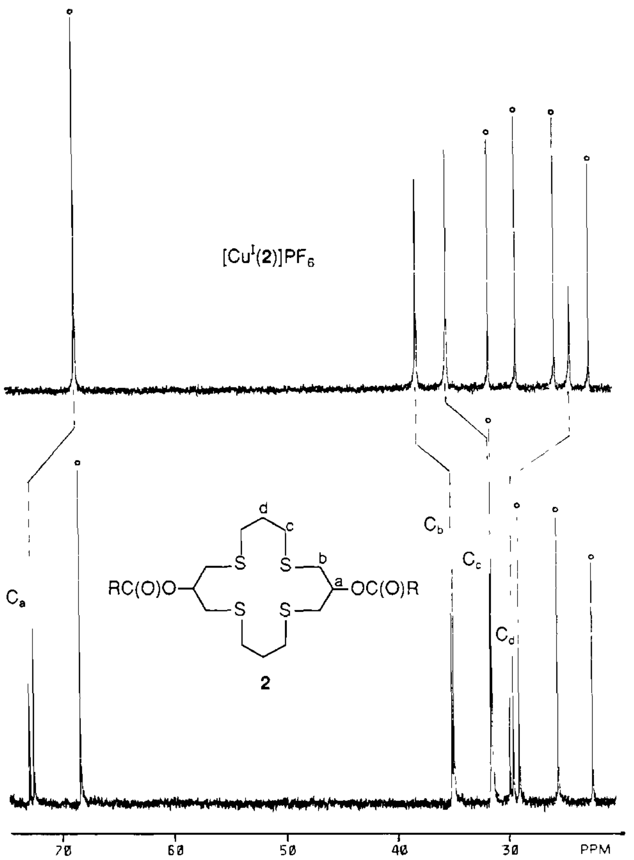


Fig. 1. 75.5 MHz $^{13}C\{^1H\}$ NMR spectra (CDCl$_3$) of macrocycle **2** and [Cu$^I$(**2**)]PF$_6$ in the region of methylene carbons. ° = Methylene tail carbons.

are devoid of mesomorphism. Whereas the absence of mesomorphism for **2** can be reasonably ascribed to the lack of a fairly rigid central core, the same reason cannot account for the similar behaviour of [Cu$^I$(**2**)]PF$_6$. Core rigidification of saturated macrocyclic ligands through metal coordination is indeed a way to induce mesomorphism [2, 3c] and failure to achieve the latter must be for additional reasons.

Provided the hydrocarbon tails are extended in opposite directions (as we would expect for the free ligand), the molecule should have an approximately linear (or rod-like) shape with a good length-to-breadth ratio. However, the possible curling of the aliphatic chains (induced by core reorganisation upon coordination) could lead to an increase of the breadth of the cation and therefore destabilisation of a mesophase. On the other hand, the presence of an isomeric mixture [7] or the ionic nature of the complex [8] is not at all an obstacle toward the formation of mesophases.

Given the above results, we are now exploring the possibility of synthesising ligands with either different cores or substituents. The choice of metal ions other than Cu(I) could also ensure a less pronounced change in the resulting molecular shape of the complexes as compared to the ligand's shape.

## Acknowledgements

Financial support from the Italian Ministero per l'Università e la Ricerca Scientifica e Tecnologica (MURST) is gratefully acknowledged. We would like to thank Professor G. Sindona for the mass spectrum.

## References

1 (a) A.M Giroud-Godquin and P.M. Maitlis, *Angew. Chem, Int Ed. Engl, 30* (1991) 375; (b) P. Espinet, M.A. Esteruelas, L.A. Oro, J.L. Serrano and E. Sola, *Coord. Chem. Rev., 117* (1992) 215; (c) S.A. Hudson and P.M. Maitlis, *Chem. Rev., 93* (1993) 861.
2 F. Neve and M. Ghedini, *J Incl. Phenom, 15* (1993) 259.
3 (a) J.M. Lehn, J. Malthête and A.M. Levelut, *J. Chem. Soc., Chem. Commun,* (1985) 1794; (b) S.H.J. Idziak, N.C. Maliszewskyj, P.A. Heiney, J.P. McCauley, Jr., P.A. Sprengler, and A.B. Smith III, *J. Am. Chem Soc., 113* (1991) 7666; (c) A. Liebmann, C. Mertesdorf, T. Plesnivy, H. Ringsdorf and J.H. Wendorff, *Angew Chem, Int Ed Engl., 30* (1991) 1375.
4 (a) A.J. Blake and M. Schroder, *Adv Inorg Chem., 35* (1990) 1; (b) S.R. Cooper and S.C. Rawle, *Struct Bonding (Berlin), 72* (1990) 1.
5 H. Tsukube, K. Takagi, T. Higashiyama, T. Iwachido and N. Hayama, *Tetrahedron Lett., 26* (1985) 881.
6 M.J. Martin, J.F. Endicott, L.A. Ochrymowycz and D.B. Rorabacher, *Inorg. Chem, 26* (1987) 3012.
7 (a) M. Ghedini, S. Armentano and F. Neve, *Inorg. Chim. Acta, 134* (1987) 23; (b) M. Ghedini, S. Armentano, F. Neve and S. Licoccia, *J. Chem. Soc., Dalton Trans,* (1988) 1565.
8 (a) H. Adams, N.A. Bailey, D.W. Bruce, S.C. Davis, D.A. Dunmur, P.D. Hempstead, S.A. Hudson and S. Thorpe, *J. Mater. Chem, 2* (1992) 395; (b) M. Marcos, M.B. Ros, J.L. Serrano, M.A. Esteruelas, E. Sola, L.A. Oro and J. Barbera, *Chem. Mater, 2* (1990) 748; (c) M. Ghedini and D. Pucci, *J Organomet. Chem., 395* (1990) 105.