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Pyridine-Based Macrocycles Containing N, O, and S and Their Use as Ion-Selective Electrodes. Crystal Structures of 15-Aza-6-oxa-3,9-dithiabicyclo[9.3.1]pentadeca-1(15),11,13-triene and (15-Aza-6-oxa-3,9-dithiabicyclo[9.3.1]pentadeca-1(15),11,13-triene)dichlorocopper(II)

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Three pyridine-based, macrocyclic, oxygen-, nitrogen-, and sulfur-containing ligands, 15-aza-6-oxa-3,9-dithiabicyclo[9.3.1]pentadeca-1(15),11,13-triene, 18-aza-6,9-dioxa-3,12-dithiabicyclo[12.3.1]octadeca-1(18),14,16-triene, and 21-aza-6,9,12-trioxa-3,15-dithiabicyclo[15.3.1]heneicosa-1(21),17,19-triene, are reported. The molecular and crystal structure of the 15-aza-6-oxa-3,9-dithiabicyclo[9.3.1]pentadeca-1(15),11,13-triene was solved by X-ray diffraction methods; the space group is monoclinic, $P2_1/c$, with $a = 9.048$ (1) Å, $b = 15.315$ (2) Å, $c = 9.565$ (2) Å, $\beta = 116.52$ (1)°, $V = 1186$ (2) Å^3, $Z = 4$, d(calcd) = 1.352 g·cm^{-3}, and $\mu = 4.05$ cm^{-1}. Its molecular structure is compared with that found by molecular mechanics calculations using the MM2 program. Complexes with Cu(II), Ni(II), and Co(II) metal ions are also reported. The molecular structure of the (15-aza-6-oxa-3,9-dithiabicyclo[9.3.1]pentadeca-1(15),11,13-triene)dichlorocopper(II) complex is described; the space group is monoclinic, $P2_1/n$, with $a = 7.381$ (1) Å, $b = 13.916$ (3) Å, $c = 14.336$ (6) Å, $\beta = 100.10$ (2)°, $V = 1449$ (2) Å^3, $Z = 4$, d(calcd) = 1.720 g·cm^{-3}, and $\mu = 21.5$ cm^{-1}. Neutral mobile carrier based liquid membrane electrodes have been prepared by using 15-aza-6-oxa-3,9-dithiabicyclo[9.3.1]pentadeca-1(15),11,13-triene as the sensor material, and their potentiometric response toward Cu(II), Ni(II), and Co(II) is also reported.

Introduction

New acyclic, pyridine-based, tridentate NS$_2$ ligands, 2,6-bis((ethylthio)methyl)pyridine, 2,6-bis(((methoxycarbonylethyl)thio)methyl)pyridine, 2,6-bis((benzylthio)methyl)pyridine, and their Zn, Cd, Cu, Co, and Ni complexes were reported by us. For the (2,6-bis((ethylthio)methyl)pyridine)dibromozinc(II)[1] and (2,6-bis((ethylthio)methyl)pyridine)dichlorocopper(II)[2] complexes, a mononuclear, pentacoordinated structure was found. For (2,6-bis((ethylthio)methyl)pyridine)dichlorocadmium(II)–water and the analogous Co(II) complex,[3] dinuclear structures were found where the metal ion is in an octahedral arrangement coordinated by the NS$_2$ moiety of the ligand and bridging chlorine atoms.

Three closely related, macrocyclic, tridentate, pyridine derivative NS$_2$ ligands, 16-aza-3,10-dithiabicyclo[10.3.1]hexadeca-1-(16),12,14-triene, 14-aza-3,8-dithiabicyclo[8.3.1]tetradeca-1-(14),10,12-triene, 13-aza-3,7-dithiabicyclo[7.3.1]trideca-1-(13),9,11-triene, were also reported by us.[2] All of them contain the same coordinating elements, (NS$_2$), structurally placed in the same fashion, sulfur–methylene–pyridine–methylene–sulfur, while the macrocyclic chain is purely aliphatic in these cases. The molecular structure of (16-aza-3,10-dithiabicyclo[10.3.1]hexadeca-1(16),12,14-triene)dichlorocopper(II) shows a distorted-trigonal-bipyramid geometry (TBP) around the metal ion, analogous to that found in the Cu(II) and Zn(II) complexes of the acyclic ligands.

In this paper we have extended our studies on these NS$_2$ macrocyclic ligands. We have connected the sulfur–pyridine–sulfur moiety with an oxygen-containing aliphatic chain, in order to elucidate the influence of the additional oxygen atoms on the chemical selectivity and complex syntheses. Thus, we report here on the syntheses of three macrocyclic oxygen- and NS$_2$-containing ligands: 15-aza-6-oxa-3,9-dithiabicyclo[9.3.1]pentadeca-1-(15),11,13-triene, 18-aza-6,9-dioxa-3,12-dithiabicyclo[12.3.1]-octadeca-1(18),14,16-triene, 21-aza-6,9,12-trioxa-3,15-dithiabicyclo[15.3.1]heneicosa-1(21),17,19-triene, and their Cu(II), Ni(II), and Co(II) complexes.

We are interested in the properties of these [NS$_2$], [NS$_2$O], [NS$_2$O$_2$], or [NS$_2$O$_3$] macrocycles as neutral carriers.[4] These molecules have soft and hard coordination sites, giving complexes with some transition-metal ions in "free solution". With them, we could expect to get specific "molecular recognition" with transition-metal ions in carrier-assisted membranes. We report in this paper on their use as neutral carriers in neutral-carrier-based ion-selective electrodes.

It is important to know the molecular structure of the receptor macrocycles and their complexes in order to understand the complex mechanism of the "molecular recognition". It is not always easy to get well-formed single crystals of these macrocycle compounds; for this reason, we think it is important to test the reliability of the molecular mechanics methods to predict the most stable conformation of these molecules. So, we also report the theoretical calculations using the MM2 program for these macrocycles, as is usual in this kind of study.

Experimental Section

Unless specifically mentioned, the syntheses of all ligands and complexes were performed under a nitrogen atmosphere, using dehydrated and deoxygenated solvents. Solvents were placed under vacuum to eliminate the dissolved oxygen.

Microanalyses (C, H, N) were performed in our analytical laboratory on a Perkin-Elmer 240-B instrument. ^{1}H NMR spectra were run on a Bruker WP80 54 instrument in CDCl$_3$ solution. Electronic spectra were performed on a Kontron-Uvikon 860 spectrophotometer in CH$_2$Cl$_2$ solution. IR spectra were recorded on a Perkin-Elmer 1710 FT spectrophotometer as KBr pellets. Mass spectrometry was performed on a Hewlett-Packard HP2985 GC/MS System Instrument.

Synthesis of 2,6-Bis(bromomethyl)pyridine. This compound was synthesized as reported in the literature.[5]

Synthesis of Polyethylene Thiodiglycol Compounds. Di-, tri-, and tetraethylene thiodiglycols were synthesized as reported in the literature.[6]

Synthesis of the Macrocyclic Ligands. Two solutions, A and B, were mixed under high dilution conditions (nitrogen atmosphere, constant stirring, 3 mL/h) over 1.5 L of dry and degassed refluxing 1-butanol.

15-Aza-6-oxa-3,9-dithiabicyclo[9.3.1]pentadeca-1(15),11,13-triene (MO1): solution A, 2,6-bis(bromomethyl)pyridine (5.3 g) in degassed 1-butanol (50 mL); solution B, diethylene thiodiglycol (2.9 g, 96%) and

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(1) Teixidor, F.; Escriche, Ll.; Casabó, J.; Molins, E.; Miravitlles, C. *Inorg. Chem.* **1986**, *25*, 4060.

(2) Escriche, Ll.; Sanz, M.; Casabó, J.; Teixidor, F.; Molins, E.; Miravitlles, C. *J. Chem. Soc., Dalton Trans.* **1989**, 1739.

(3) Teixidor, F.; Escriche, Ll.; Rodríguez, I.; Casabó, J.; Rius, J.; Molins, E.; Martínez, B.; Miravitlles, C. *J. Chem. Soc., Dalton Trans.* **1989**, 1381.

(4) Koryta, J. *Anal. Chim. Acta* **1984**, *159*, 1.

(5) Vögthel, F.; Offerman, W. *Synthesis* (*Commun.*) **1972**, 122.

(6) *Organicum: Practical Handbook of Organic Chemistry*, Hazzard, B. J., Ed.; Pergamon Press Ltd.: Oxford, England, 1973.

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[‡] Institut de Ciència dels Materials (CSIC).

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Table I. Analytical and Physical Data

compound	color	% yield	% C found/calcd	% N found/calcd	% H found/calcd	solv[a]	λ[b]	ν(C–O–C)[c]
MO1	white	6.3	55.3/54.77	5.8/5.81	6.3/6.22		274, 212	1067
MO2	white	9.0	54.5/54.74	4.7/4.91	6.7/6.66		273, 214	1088, 1104
MO3	white	8.0	*d*	*d*	*d*		271, 213	1117
Cu(MO1)Cl_2	green	40.0	35.8/35.15	3.7/3.73	4.0/3.99	a	796	1021, 1123
Ni(MO1)Cl_2	green	88.0	35.6/35.58	3.7/3.77	4.0/4.04	b	654	1016, 1090
Ni(MO1)$(SCN)_2$	blue	83.0	36.9/37.50	9.6/10.09	3.6/3.60	a	593	1014, 1084
Co(MO1)Cl_2	pink	86.0	35.4/35.58	3.8/3.77	4.0/4.04	b	630	1018, 1091
Co(MO1)$(SCN)_2$	pink	80.0	37.7/37.50	9.6/10.09	3.4/3.60	a	511	1018, 1085
Cu(MO2)Cl_2	green	40.0	36.6/37.18	3.1/3.30	4.5/4.52	b	715	1038, 1096, 1130
Cu(MO2)Br_2	green	40.0	30.7/30.68	2.7/2.75	3.6/3.74	a	788	1037, 1096, 1132
Ni(MO2)$(SCN)_2$	blue	40.0	39.3/39.73	8.9/9.13	4.0/4.13	c	593	1041, 1094, 1133
Co(MO2)$(SCN)_2$	blue	40.0	40.3/39.73	8.5/9.13	4.3/4.13	c	627	1042, 1094, 1133

[a] Solvent used in the synthesis: (a) methanol; (b) methanol/ethyl acetate, 2/3, (c) methanol/ethyl acetate, 1/1. [b] Electronic spectra in solid state (diffuse reflectance), nm; except for free ligands, CH_2Cl_2 solution. [c] C–O–C IR stretching frequencies, cm^{-1}. [d] Values not available due to the oily liquid state characteristic of the compound.

K(OH) (2.25 g) in degassed 1-butanol (50 mL).

18-Aza-6,9-dioxa-3,12-dithiabicyclo[12.3.1]octadeca-1(18),14,16-triene (MO2): solution A, 2,6-bis(bromomethyl)pyridine (5.3 g) in degassed 1-butanol (50 mL); solution B, triethylene thiodiglycol (4.2 g, 90%) and K(OH) (2.25 g) in degassed 1-butanol (50 mL).

21-Aza-6,9,12-trioxa-3,15-dithiabicyclo[15.3.1]heneicosa-1(21),17,19-triene (MO3): solution A, 2,6-bis(bromomethyl)pyridine (5.3 g) in degassed 1-butanol (50 mL); solution B, tetraethylene thiodiglycol (4.84 g, 93%), K(OH) (2.25 g) in degassed 1-butanol (50 mL).

In all cases, the mixture was allowed to reflux for 2 h after the addition was concluded (17 h). A white precipitate of KBr which was obtained was discarded. The clear solution was evaporated until a dark oil appeared. The oil was extracted with benzene (150 mL), and the extract was washed with a Na_2CO_3 solution (twice) and H_2O (twice) and dried with Na_2SO_4 (8 h). The benzene solution was evaporated, and the reddish oil obtained was dissolved in benzene (5 mL) and chromatographed over neutral alumina using benzene as an eluent. The first collected fraction was evaporated to yield a yellowish oil.

MO1 Macrocycle. To the aforementioned yellowish oil was added petroleum ether (50 mL; 40–60 °C), and a white solid of MO1 precipitated.

MO2 Macrocycle. The yellowish oil was dissolved in petroleum ether (50 mL; 40–60 °C) and the solution was kept in the freezer. A white solid was obtained (sometimes it was necessary to scratch the beaker's interior with a glass rod), which was filtered off, washed, and dried under vacuum.

MO3 Macrocycle. The yellowish oil was dissolved in petroleum ether (50 mL; 40–60 °C), and the solution was kept in the freezer. A colorless liquid appeared, which was the MO3 compound. The liquid was dried under vacuum for 3 h.

Spectral Data. 15-Aza-6-oxa-3,9-dithiabicyclo[9.3.1]pentadeca-1(15),11,13-triene (MO1). ^1H NMR ($CDCl_3$): δ 2.7 (t, 4 H, R–CH_2–S–R′), 3.4 (t, 4 H, R–CH_2–O–R′), 3.8 (s, 4 H, Ar–CH_2–S), 7.5 (m, 3 H, ArH). Mass spectrum; *m/e* 241 (40%) [M^+]. IR (KBr): ν(C–O–C), 1067 cm^{-1}. Electronic spectrum (CH_2Cl_2): 274 nm (ε = 3980), 212 nm (ε = 7890).

18-Aza-6,9-dioxa-3,12-dithiabicyclo[12.3.1]octadeca-1(18),14,16-triene (MO2). ^1H NMR ($CDCl_3$): δ 2.7 (t, 4 H, R–CH_2–S–R′), 3.4 (t + s, 8 H, R–CH_2–O–R′, O–CH_2–CH_2–O), 3.8 (s, 4 H, Ar–CH_2–S), 7.5 (m, 3 H, ArH). Mass spectrum: *m/e* 285 (20%) [M^+]. IR (KBr): ν(C–O–C), 1088, 1104 cm^{-1}. Electronic spectrum (CH_2Cl_2): 273 nm (ε = 4120), 214 nm (ε = 7640).

21-Aza-6,9,12-trioxa-3,15-dithiabicyclo[15.3.1]heneicosa-1(21),17,19-triene (MO3). ^1H NMR ($CDCl_3$): δ 2.7 (t, 4 H, R–CH_2–S–R′), 3.4 (t + s, 12 H, R–CH_2–O–R′, O–CH_2–CH_2–O), 3.8 (s, 4 H, Ar–CH_2–S), 7.5 (m, 3 H, ArH). Mass spectrum: *m/e* 329 (5%) [M^+]. IR (KBr): ν(C–O–C), 1117 cm^{-1}. Electronic spectrum (CH_2Cl_2): 271 nm (ε = 4090), 213 nm (ε = 7645).

Complexes of the Macrocyclic Ligands. Equimolecular solutions of the appropriate ligand and metal salts in methanol were mixed in all cases. In a typical experiment, MO1 (0.4 g, 1.7 × 10^{-3} mmol) dissolved in methanol (5 mL) was added to a solution of $CuCl_2 \cdot 2H_2O$ (0.37 g, 1.7 × 10^{-3} mmol) in methanol (5 mL). A green precipitate separated and was filtered off, washed with methanol and vacuum-dried. The solvent used depended upon the compound synthesized (Table I).

Table I reports the physical and analytical data for the synthesized compunds.

X-ray Structure Determination. By slow cooling of a solution of the MO1 compound in tetrahydrofruan, colorless, well-formed crystals suitable for X-ray analysis were obtained. By slow diffusion of dry tetrahydrofuran into a methanolic solution of the Cu(MO1)Cl_2 complex, green, prismatic, well-formed crystals were obtained.

Table II. Crystal Data and Details of the Intensities Collection

	MO1	Cu(MO1)Cl_2
(A) Crystal Parameters at 293 K		
empirical formula	$C_{11}H_{15}NOS_2$	$C_{11}H_{15}NOS_2CuCl_2$
mol wt	241.1	375.7
space group	$P2_1/c$	$P2_1/n$
a, Å	9.048 (1)	7.381 (1)
b, Å	15.315 (2)	13.916 (3)
c, Å	9.565 (2)	14.336 (6)
β, deg	116.52 (1)	100.10 (2)
V, $Å^3$	1186 (2)	1449 (2)
d(calcd), $g \cdot cm^{-3}$	1.352	1.720
abs coeff (μ), cm^{-1}	4.05	21.5
Z	4	4
cryst dimen, nm	0.3 × 0.3 × 0.15	0.3 × 0.35 × 0.5
F(000)	512	764
(B) Data Measurement Parameters		
radiation	Mo Kα (λ = 0.71069 Å)	Mo Kα (λ = 0.71069 Å)
no. of colled reflcns	2314	2827
no. of unique reflcns	2082	2555
no. of obsd reflcns	1650 [$I > 2.5\sigma(I)$]	2023 [$I > 2\sigma(I)$]
data collcn range, 2θ	0–50	2–50
scan method	ω–2θ	ω–2θ
range of *hkl*	–9, 9; 0, 18; 0, 10	–8, 8; 0, 16; 0, 17
std reflcn decay, %	0.9	1.2
(C) Data Refinement Parameters		
no. of refined params	183	173
R, %	3.5	4.2
R_w,[a] %	4.1	4.4
max final diff Fourier peak, e·$Å^3$	0.27	0.4
min final diff Fourier peak, e·$Å^3$	–0.18	–0.2
largest shift/esd final cycle	0.31	0.25

[a] $w = 1/[\sigma^2(F) + 0.001244F^2]$.

X-ray diffraction data for the MO1 and Cu(MO1)Cl_2 compounds were collected with an Enraf-Nonius CAD4 four-circle diffractometer. The diffraction intensities were corrected for Lorentz and polarization effects.

Both structures were solved by direct methods.[7] Subsequent difference Fourier syntheses combined with refinement of located atoms performed the complete model of the structure. This model was refined with Shelx76[8] by using anisotropic thermal parameters. The hydrogen atoms were introduced in calculated positions and refined with global temper-

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(7) Main, P.; Fiske, S. J.; Hull, S. E.; Lessinger, L.; Germain, G.; Declercq, J. P.; Woolfson, M. M. Multan-82. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data. Universities of York, England and Louvain, Belgium.

(8) Sheldrick, G. M. Programs for Crystal Structure Determination. University of Cambridge, England, 1976.

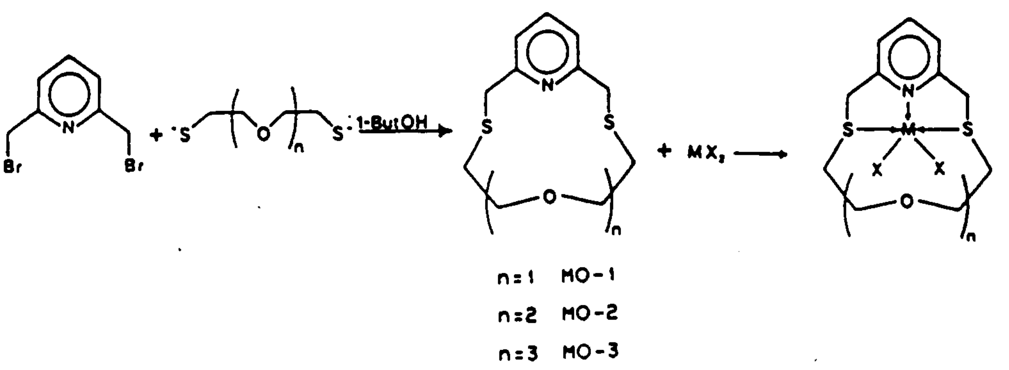

Figure 1. General synthetic procedure scheme.

ature factors. The scattering factors were taken from ref 9. Table II reports the X-ray data analysis.

Theoretical Calculations on Isolated Ligands. Molecular mechanics calculations on MO1 and MO2 macrocycles were run on a VAX-8800 minicomputer at the Computer Centre of the Universitat Autònoma de Barcelona by using a local version of Allinger's MM2(77) program.[10,11] Torsional energy surfaces were covered by using the two bond-drive technique with 15° steps, starting at dihedral angle values of −180° and ending at 180°. The large size of MO3 (21 heavy atoms and a 18-membered ring) forced us to abandon the theoretical study of it.

Construction and Calibration of the Neutral Mobile Carrier PVC Membrane Electrodes. The sensor membranes were prepared and assembled as previously described.[12-14] The sensor material (macrocycles, 7%) with dioctyl phthalate (31%) as plasticizer and poly(vinylchloride) (62%) were dissolved in tetrahydrofuran. The sensor solution was dropped on a conductive circular flat cavity (0.2 mm deep) drilled in the end of an electrode tube sealed with a layer of a conducting polymer material. The conductive material (graphite-loaded epoxy resin), which was used as the solid internal contact of the membrane electrode, has been described previously.[13,14] The electrode was usually conditioned before use by soaking it for 24 h in a 10^{-3} M copper(II) chloride solution.

The response characteristics, the response time of the constructed membrane electrodes, and the selectivity coefficients $K^{pot}_{A,B}$ were determined by the reported standard methods.[15] The following electrochemical cell was used for measuring the membrane potentials: solid internal contact/sensor membrane/working solution/reference electrode. The emf was measured relative to a Ag–AgCl double-junction reference electrode (Orion 90-02-00) with the outer chamber filled with 10^{-1} M potassium nitrate solution. A Crison (Barcelona, Spain) digital potentiometer (±0.1 mV) was used. All measurements were carried out at 25 ± 0.1 °C.

Results and Discussion

The general synthetic procedure used to prepare the macrocyclic ligands and their complexes is shown in Figure 1. The solubility of the macrocycles in low-polarity solvents increases as the length of the corresponding aliphatic chain increases. The MO3 compound is an oily liquid soluble in petroleum ether, and in no case has it been possible to isolate well-characterized complexes with it.

Crystal and Molecular Structure of (15-Aza-6-oxa-3,9-dithiabicyclo[9.3.1]pentadeca-1(15),11,13-triene)dichlorocopper(II) (Cu(MO1)Cl$_2$). Figure 2 shows the atom numbering and a view of the molecule. Table III reports the fractional atomic coordinates for the non-hydrogen atoms. Table IV shows selected bond distances and angles for the molecule.

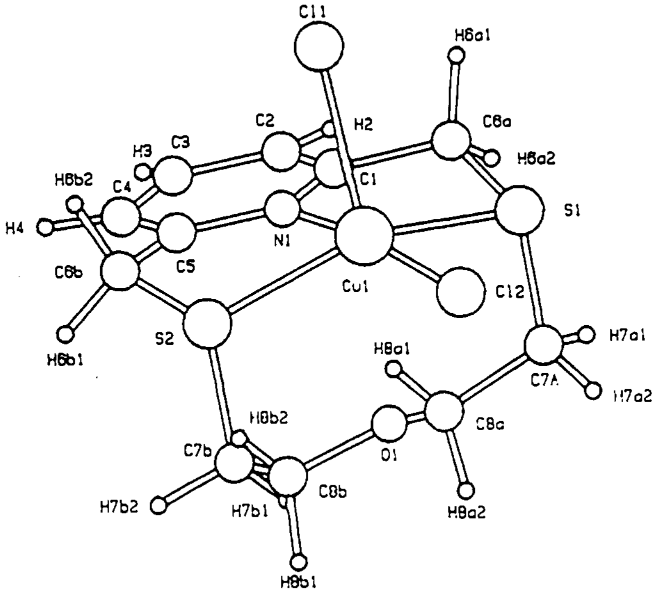

Figure 2. Perspective view of the 15-aza-6-oxa-3,9-dithiabicyclo[9.3.1]pentadeca-1(15),11,13-triene (MO1) compound with the atom numbering.

Table III. Fractional Atomic Coordinates for Non-Hydrogen Atoms ($\times 10^4$) with Their Esd's and Equivalent Temperature Factors for (15-Aza-6-oxa-3,9-dithiabicyclo[9.3.1]pentadeca-1(15),11,13-triene)dichlorocopper(II) (Cu(MO1)Cl$_2$)

	x/a	y/b	z/c	B_{eq}, Å^2
Cu1	6708.9 (0.7)	1185.8 (0.4)	2896.8 (0.4)	2.90
Cl1	8635 (2)	1747 (1)	1738 (1)	3.73
Cl2	8280 (2)	1777 (1)	4269 (1)	4.26
S1	4447 (2)	2409 (1)	2759 (1)	3.56
S2	7877 (2)	−375 (1)	3202 (1)	3.81
N1	5018 (5)	576 (2)	1790 (2)	2.69
C1	3615 (6)	1088 (3)	1293 (3)	3.07
C2	2425 (6)	690 (4)	554 (3)	3.85
C3	2660 (7)	−255 (4)	304 (4)	4.24
C4	4090 (7)	−775 (4)	812 (3)	3.66
C5	5249 (6)	−350 (3)	1548 (3)	2.98
C6a	3420 (6)	2124 (3)	1565 (3)	3.59
C6b	6879 (7)	−883 (3)	2073 (3)	3.72
C7a	2790 (6)	1935 (4)	3444 (3)	3.88
C8a	2575 (7)	855 (4)	3434 (4)	4.05
O1	4321 (4)	455 (2)	3794 (2)	3.65
C7b	6415 (9)	−829 (4)	3992 (4)	4.82
C8b	4418 (8)	−566 (3)	3760 (4)	4.50

In this complex, the copper atom is clearly coordinated by the N and the S atoms of the macrocycle and two chlorine atoms in a square-pyramidal fashion. It is interesting to compare this complex with (2,6-bis((ethylthio)methyl)pyridine)dichlorocopper(II).[2] In the last compound, the acyclic ligand has the coordinating sites (NS$_2$) in an arrangement identical with that found in the macrocyclic molecule. The Cu–N and Cu–S distances in both complexes are similar (2.016 Å and 2.344 and 2.358 Å in the acyclic ligand complex; 2.024 Å and 2.369 and 2.350 Å in the macrocyclic one). Two different Cu–Cl distances are found, the Cu–Cl2 (2.255 Å) distance being smaller than the Cu–Cl1

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(9) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. 4, p 99.

(10) Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 8127.

(11) Allinger, N. L.; Yuh, N. Y. *QCPE* **1980**, *12*, 395.

(12) Alegret, S.; Alonso, J.; Bartrolí, J.; Paulís, J. M.; Lima, J. L. F. C.; Machado, A. A. S. C. *Anal. Chim. Acta* **1984**, 164, 147.

(13) Alegret, S.; Alonso, J.; Bartrolí, J.; Lima, J. L. F. C.; Machado, A. A. S. C. *Proceedings of the 2nd International Meeting of Chemical Sensors*, Auconturier, J. L., et al., Eds.; Bordeaux Chemical Sensors: Talance, France, 1986; p 751.

(14) Alegret, S.; Martínez-Fàbregas, E. *Biosensors* **1989**, *4*, 287.

(15) *Compendium of Analytical Nomenclature*; Pergamon Press: Oxford, England, 1978; pp 168–173.

Table IV. Selected Bond Lengths (Å) and Angles (deg) with Their Esd's for (15-Aza-6-oxa-3,9-dithiabicyclo[9.3.1]pentadeca-1(15),11,13-triene)dichlorocopper(II) (CuMO1)Cl_2)

Cl1–Cu1	2.495 (1)	C2–C1	1.369 (6)
Cl2–Cu1	2.255 (1)	C6a–C1	1.507 (6)
S1–Cu1	2.369 (1)	C3–C2	1.381 (7)
S2–Cu1	2.350 (1)	C4–C3	1.377 (7)
N1–Cu1	2.024 (3)	C5–C4	1.370 (6)
C6a–S1	1.790 (5)	C6b–C5	1.498 (6)
C7a–S1	1.822 (5)	C8a–C7a	1.510 (7)
C6b–S2	1.799 (5)	O1–C8a	1.415 (6)
C7b–S2	1.811 (6)	C8b–O1	1.425 (6)
C1–N1	1.352 (5)	C8b–C7b	1.498 (8)
C5–N1	1.353 (5)		
Cl2–Cu1–Cl1	101.6 (1)	C5–N1–C1	119.1 (4)
S1–Cu1–Cl1	101.3 (1)	C2–C1–N1	121.4 (4)
S1–Cu1–Cl2	93.3 (1)	C6a–C1–N1	117.9 (4)
S2–Cu1–Cl1	100.4 (1)	C6a–C1–C2	120.7 (4)
S2–Cu1–Cl2	93.4 (1)	C3–C2–C1	119.5 (5)
S2–Cu1–S1	155.6 (1)	C4–C3–C2	118.9 (5)
N1–Cu1–Cl1	87.4 (1)	C5–C4–C3	119.7 (5)
N1–Cu1–Cl2	171.0 (1)	C4–C5–N1	121.3 (4)
N1–Cu1–S1	84.7 (1)	C6b–C5–N1	117.9 (4)
N1–Cu1–S2	85.0 (1)	C6b–C5–C4	120.7 (4)
C6a–S1–Cu1	95.4 (2)	C1–C6a–S1	114.6 (3)
C7a–S1–Cu1	103.0 (2)	C5–C6b–S2	115.0 (3)
C7a–S1–C6a	102.9 (2)	C8a–C7a–S1	115.8 (3)
C6b–S2–Cu1	96.7 (1)	O1–C8a–C7a	107.5 (4)
C7b–S2–Cu1	101.5 (2)	C8b–O1–C8a	115.3 (4)
C7b–S2–C6b	103.4 (3)	C8b–C7b0–S2	116.6 (4)
C1–N1–Cu1	120.1 (3)	C7b–C8b–O1	106.8 (4)
C5–N1–Cu1	120.8 (3)		

(2.495 Å) distance. Similar differences in the distances to the apical and basal chlorine atoms are found in the aforementioned (16-aza-3,10-dithiabicyclo[10.3.1]hexadeca-1(16),12,14-triene)-dichlorocopper(II) complex. One interesting fact to note is that the S1-N-S2 angle is similar in both complexes (101.9 and 102.9°), indicating that equivalent cavities are available for the metal ions in both ligands.

The oxygen ether atom O1 of the macrocyclic ligand is separated 2.568 Å from the copper atom. This distance is larger than a typical Cu–O bond length, but it provides a sixth coordination position, which is normal for a large number of pseudooctahedral copper complexes.[16,17] The N1, S1, S2, Cl1, and Cl2 atoms display a distorted square-pyramidal coordination polyhedron. The N1 and Cl2 atoms deviate 0.198 and 0.097 Å above the mean plane determined by the N1, Cl2, S1, and S2 atoms. On the other hand, the S1 and S2 atoms deviate 0.143 and 0.152 Å below the same plane. The Cu atom is located 0.317 Å above and the apical Cl1 atom is 14.8° from the perpendicular to the aforementioned mean plane. In the copper complex of the acyclic ligand 16-aza-3,10-dithiabicyclo[10.3.1]hexadeca-1(16),12,14-triene, the basal chlorine atom deviates only 0.017 Å from the plane defined by N, S1, S2, and Cl2, and the apical chlorine atom is only 6.8° from the perpendicular to this plane. The larger deviations found in the macrocyclic ligand complex may be attributed to the repulsion between the oxygen ether atom of the ring and the chlorine atom Cl2. These repulsions force both the Cl1 and Cl2 atoms to move from the ideal position. It is interesting to note that the Cl1–Cu–Cl2 angles are similar in the acyclic and macrocyclic complexes (101.9 and 102.9°). The O1 atom deviates only 5.7° from the perpendicular to the mean plane defined by N1, S1, S2, and Cl2. In conclusion, the coordination polyhedron around the Cu(II) ion can be considered as a distorted octahedron, as is common in copper(II) complexes. It is worth noticing here the virtual planarity of the chain determined by the atoms O1, C7b, C8b, C8a and C7a. The corresponding deviations (Å) from the mean plane defined by these atoms are as follows: O1, 0.117; C7b, –0.055; C8b, 0.011; C8a, –0.043; C7a, –0.029. This chain conformation is unusual in crown ether like compounds. To better understand this apparent singularity, the molecular structure of the free ligand was solved by X-ray methods.

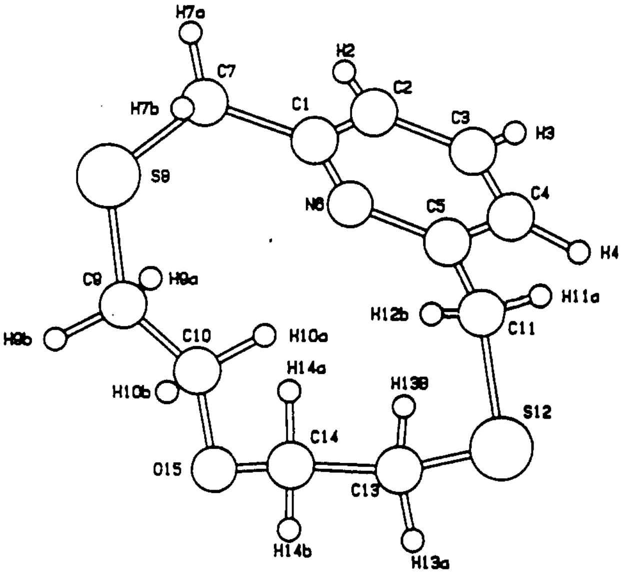

Figure 3. Perspective view of the (15-aza-6-oxa-3,9-dithiabicyclo-[9.3.1]pentadeca-1(15),11,13-triene)dichlorocopper(II) (Cu(MO1)Cl_2) compound with the atom numbering.

Table V. Fractional Atomic Coordinates for Non-Hydrogen Atoms (×10^4) with Their Esd's and Equivalent Temperature Factors for 15-Aza-6-oxa-3,9-dithiabicyclo[9.3.1]pentadeca-1(15),11,13-triene (MO1)

	x/a	y/b	z/c	B_{eq}, Å^2
C1	7477 (3)	4702 (2)	8352 (3)	3.31
C2	7755 (4)	5057 (2)	7157 (4)	4.32
C3	9066 (4)	4752 (2)	6937 (4)	4.80
C4	10056 (4)	4104 (2)	7894 (4)	4.37
C5	9699 (3)	3776 (2)	9062 (3)	3.35
N6	8425 (3)	4072 (1)	9294 (3)	3.12
C7	6060 (4)	4996 (2)	8650 (4)	4.23
S8	4085 (1)	4498 (1)	7352 (1)	4.55
C9	4532 (4)	3353 (2)	7869 (4)	4.57
C10	5070 (4)	2896 (2)	6797 (4)	4.44
C11	10693 (4)	3065 (2)	10147 (4)	4.24
S12	10531 (1)	2002 (1)	9219 (1)	4.56
C13	8385 (4)	1956 (2)	7769 (4)	4.57
C14	7184 (5)	1922 (2)	8475 (5)	4.75
O15	5522 (2)	2005 (1)	7259 (3)	5.04

Table VI. Selected Bond Lengths (Å) and Angles (deg) with Their Esd's for 15-Aza-6-oxa-3,9-dithiabyclco[9.3.1]pentadeca-1(15),11,13-triene (MO1)

C2–C1	1.386 (3)	S8–C7	1.826 (3)
N6–C1	1.338 (3)	C9–S8	1.818 (3)
C7–C1	1.501 (3)	C10–C9	1.492 (4)
C3–C2	1.375 (4)	O15–C10	1.436 (3)
C4–C3	1.376 (4)	S12–C11	1.829 (2)
C5–C4	1.388 (3)	C13–S12	1.815 (2)
N6–C5	1.346 (3)	C14–C13	1.515 (4)
C11–C5	1.496 (3)	O15–C14	1.438 (3)
N6–C1–C2	122.7 (2)	S8–C7–C1	113.9 (2)
C7–C1–C2	121.6 (2)	C9–S8–C7	100.7 (1)
C7–C1–N6	115.6 (2)	C10–C9–S89	111.5 (2)
C3–C2–C1	118.7 (2)	O15–C10–C9	111.8 (2)
C4–C3–C2	119.6 (2)	S12–C11–C5	114.7 (2)
C5–C4–C3	118.6 (2)	C13–S12–C11	103.4 (1)
N6–C5–C4	122.4 (2)	C14–C13–S12	113.4 (2)
C11–C5–C4	122.5 (2)	O15–C14–C13	109.6 (2)
C11–C5–N6	115.1 (2)	C14–O15–C10	112.5 (2)
C5–N6–C1	118.0 (2)		

Crystal and Molecular Structure of 15-Aza-6-oxa-3,9-dithiabicyclo[9.3.1]pentadeca-1(15),11,13-triene (MO1). Figure 3 shows

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(16) Hathaway, B. J. *Coord. Chem. Rev.* **1970**, *1*, 5.
(17) Hathaway, B. J. *Essays Chem.* **1971**, *2*, 60.

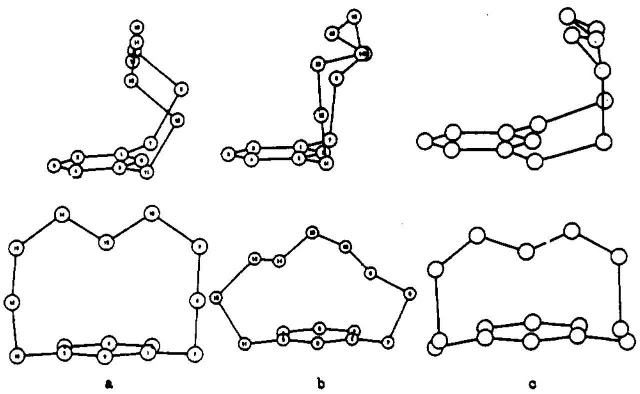

Figure 4. Perspective views of (a) the most stable conformer obtained by MM methods of the MO1 molecule, (b) the molecular structure of the MO1 molecule solved by X-ray methods, and (c) the molecular structure of the MO1 molecule in the copper complex Cu(MO1)Cl_2 solved by X-ray methods.

the atom numbering and a view of the molecule. Table V reports the fractional atomic coordinates for non-hydrogen atoms. Table VI shows selected bond distances and angles for the molecule.

The intermolecular distances and angles are typical for these kinds of organic molecules. However, certain conformational characteristics are worthy of comment. The molecule is not planar. The pyridine ring and atoms C7 and C11 lie on a plane. From this plane, C7 and C11 atoms deviate only 0.017 Å. The atoms of the aliphatic chain are located in a pseudoplane forming a dihedral angle of 78° with the pyridine ring. The reason for this nonplanarity is not clear, but it is similar to that found in the complexes of the 16-aza-3,10-dithiabicyclo[10.3.1]hexadeca-1-(16),12,14-triene-related macrocycle.[2] The most plausible explanation for the observed nonplanarity could be the repulsions between sulfur atoms, S8 and S12, evidenced by the large value of the S8–N6–S12 angle (126.8°). The sulfur–sulfur repulsions force the aliphatic chain to fold over the pyridine ring. The C10, O15, and C14 atoms are found in a plane nearly perpendicular to the aliphatic chain, as it is usual in organic ethers, very different from the conformation found in the copper complex discussed before. The metal coordination makes the S–S distance shorter in the complex than in the free ligand and could force the unusual conformation of the aliphatic chain found in the Cu(II) complex. However, both conformers (free ligand and complexed ligand) are not superimposable, and it is difficult to get conclusions out of them. To get a conformer "lattice free", we undertook a molecular mechanics study in the hope of obtaining a low-energy conformer that would be comparable to that observed in the complex. We were fortunate in observing that the most stable conformer obtained in the MM study fulfilled our expectations (Figure 4a).

Theoretical Calculations on Isolated Macrocycles. The conformational behavior of MO1 in its gaseous state was simulated by driving two different pairs of dihedral angles, w_1/w_2 (C1–C7–S8–C9/C11–S12–C13–C14 and C1–C7–S8–C9/C10–O15–C14–C13) (Figure 2).

In both cases, the most stable conformer was found to exist at C1–C7–S8–C9 = −60° and C11–S12–C13–C14 = −120°. This conformation is symmetric and nonplanar, having the saturated chain located in a plane perpendicular to the pyridine ring (Figure 4a). The aliphatic chain presents anti conformations around C–O bonds and almost gauche ones around C–C bonds as a consequence of having two terminal C atoms in the former and O and S atoms in the latter.

Figure 4 presents diagrammatically the molecular structures found by X-ray analyses of the free ligand (b) and the ligand molecule in the copper complex (c) and the most stable conformer of the macrocyclic molecule determined by MM techniques (a). The three structures have some resemblances, but those observed between structures a and c are remarkable. If we assume that upon coordination the two sulfur atoms will tend to be coplanar with the pyridine ring it is evident that Figure 4a is very similar to Figure 4c, except for the important fact that the CH_2–CH_2–O–CH_2–CH_2 plane tilts the other way. It is clear from Figure 4 that the metal coordination shortens the S–S distance and forces the sulfur atoms to lie closer the pyridine ring to assure better NS_2 coordination, and pushing the CH_2–CH_2–O–CH_2–CH_2 chain to bend over the copper(II) ion to fill the ion's sixth coordination position with the oxygen.

To summarize, we have observed an unusual disposition of the oxygen atom in the CH_2–CH_2–O–CH_2–CH_2 fragment in the copper complex. Its main characteristic is the coplanarity of the whole fragment. Due to oxygen coordination to the copper(II) ion in the complex, it was assumed that this disposition was metal forced; however, MM calculations on the free ligand showed that the most stable conformer had the same disposition, which implied that in both situations this conformation was only due to the ligand itself and not due to the oxygen coordination as could had been assumed.

The ligand MO2 contains three more atoms in the aliphatic chain, and consequently, the conformational behavior of MO2 is more complicated than that of MO1. Many conformers were obtained having relative energies smaller than 1 kcal/mol, making it difficult to assign only one to this molecule in its gaseous state and by extrapolation in its liquid state or even in solution.

Metal Complexes. Three copper complexes, Cu(MO1)Cl_2, Cu(MO2)Cl_2, and Cu(MO2)Br_2, three nickel complexes, Ni(MO1)Cl_2, Ni(MO1)$(NCS)_2$, and Ni(MO2)$(NCS)_2$, and three cobalt complexes, Co(MO1)Cl_2, Co(MO1)$(NCS)_2$, and Co(MO2)$(NCS)_2$, have been synthesized. A distorted octahedral arrangement has been shown for the metal ion where the sixth coordination position is provided by the oxygen atom of the macrocycle ring in Cu(MO1)Cl_2. This oxygen–metal interaction is confirmed for all these metal complexes by the splitting and shifting of the IR bands attributable to the ν(C–O–C) modes of the aliphatic chain,[18] with respect to the free ligand, as is reported in Table I.

The electronic spectra in the solid state are similar for all of them (Table I). There is only one band in the visible spectrum. The position of this band is typical for distorted octahedral copper(II),[16,17] nickel(II),[19] and cobalt(II) complexes.[20]

Metal–Thiocyanate Complexes. The metal–thiocyanate complexes exhibit only one band in the ν(CN) mode region, at 2074 cm^{-1} for Ni(MO1)$(NCS)_2$, 2092 cm^{-1} for Ni(MO2)$(NCS)_2$, 2071 cm^{-1} for Co(MO1)$(NCS)_2$, and 2090 cm^{-1} for Co(MO2)$(NCS)_2$. These values are typical for nitrogen-coordinated thiocyanate complexes.[21] The bands attributable to the ν(CS) and δ(NCS) modes are not visible due to the overlapping with other macrocyclic ligand bands in the corresponding zones.

Ionophore Properties of the Macrocycles. The liquid membrane electrode reported here with 15-aza-6-oxa-3,9-dithiacyclo-[9.3.1]pentadeca-1(15),11,13-triene (MO1) as sensor displays a Nernstian response for Cu(II), while Ni(II) and Co(II) may be considered as interferences with $K^{\mathrm{pot}}_{i,j} = 10^{-1}$. However, this $K^{\mathrm{pot}}_{i,j}$ value implies only a slightly better recognition for Cu(II) with respect to Ni(II) and Co(II). These results are in accord with the exocyclic characteristics of the complexes, as is evident from the X-ray diffraction study of Cu(MO1)Cl_2 reported here. Probably, the spatial disposition of the aliphatic chain in these macrocyclic compounds does not favor a good selectivity toward transition-metal ions. The differences observed are in agreement with the Irving–Williams series. On the other hand, the retention of the carrier in the PVC membrane is made difficult by the observed relatively high solubility of the complexes in water. This fact prevents the complete carrier immobilization in the membrane and reproducibility of the electrode's measurements. At the moment, we are trying to improve this characteristic by slightly modifying the functionality of the molecular structure of these

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(18) *The Infrared Spectra of Complex Molecules*, 2nd ed.; Bellamy, J., Ed.; Chapman and Hall, Ltd.: London, 1975; Vol. 1.

(19) Sacconi, L. *Transition Met. Chem.* (*N.Y.*) **1968**, *4*, 199.

(20) Carlin, R. L. *Transition Met. Chem.* (*N.Y.*) **1965**, *1*, 1.

(21) *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Nakamoto, K., Ed.; John Wiley & Sons: New York; 1986.

Table VII. Properties of Ion-Selective Membrane Electrodes

detection limit for Cu(II), M	10^{-6}
slope, mV/decade	28
response time, s	<10
selectivity coeff ($K^{pot}_{Cu,B}$)	
Ni(II)	10^{-1}
Co(II)	10^{-1}

macrocycles. The response characteristics of the electrodes in standard copper solutions are rather good, presenting near-Nernstian response, a low practical detection limit, and a short response time (Table VII).

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Registry No. MO1, 59945-48-1; MO2, 59945-49-2; MO3, 52577-37-4; Cu(MO1)Cl_2, 132673-29-1; Ni(MO1)Cl_2, 132673-30-4; Ni(MO1)$(SCN)_2$, 132673-31-5; Co(MO1)Cl_2, 132673-32-6; Co(MO1)$(SCN)_2$, 132673-33-7; Cu(MO2)Cl_2, 132673-34-8; Cu(MO2)Br_2, 132698-27-2; Ni(MO2)$(SCN)_2$, 132673-35-9; Co(MO2)$(SCN)_2$, 132673-36-0; 2,6-bis(bromomethyl)pyridine, 7703-74-4; diethylene thiodiglycol, 2150-02-9; triethylene thiodiglycol, 14970-87-7; tetraethylene thiodiglycol, 2781-02-4; Cu, 7440-50-8.

Supplementary Material Available: Tables of anisotropic thermal parameters for both compounds (2 pages); tables of observed and calculated structure factors (21 pages). Ordering information is given on any current masthead page.

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Studies of Micellar Metalloporphyrins. Synthesis and Spectroscopic Characterization of $[(P)H_2]^+$ and $[(P)M^{II}]^+$, Where P = the Dianion of 5-(4-*N*-Hexadecylpyridiniumyl)-10,15,20-triphenylporphyrin Bromide and M = VO, Ni, or Cu

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The synthesis and spectroscopic characterization of 5-(4-*N*-hexadecylpyridiniumyl)-10,15,20-triphenylporphyrin bromide (abbreviated as $[(hTriP)H_2]^+Br^-$) and its nickel, copper, and vanadyl metalated derivatives are reported. The investigated porphyrins are monomeric in neat ethanol or neat DMF, but the formation of micelles is demonstrated to occur in either ethanol–water or DMF–water mixtures containing 65–80% H_2O. UV–visible, NMR, and ESR spectroscopy and electron microscopy were used to characterize the porphyrins in both their monomeric and micellar forms. Electron microscopy of $[(hTriP)Ni]^+$ and $[(hTrip)Cu]^+$ shows that the diameter of the spherical micelles varies between 50 and 120 Å and also that these micelles decompose via further aggregation.

Introduction

Vanadium and nickel are two major metals found in crude oils. Neither metal is in an ionic form but is complexed by porphyrin macrocycles such as deoxophylloerythroetioporphyrin, etioporphyrin, and rhodoporphyrin.[2–6] A non-porphyrin fraction of nickel and vanadium may also be present,[7–9] but this has not been investigated in great detail.

The best method to quantitatively determine metalloporphyrins in crude oil involves UV–visible measurements at wavelengths of the porphyrin Soret band. This spectroscopic method is quite accurate in most cases, but low values are sometimes obtained for nonhomogeneous solutions, as recently demonstrated by an EXAFS study of asphaltenes.[10] The EXAFS spectra were strongly dominated by a pattern of vanadyl porphyrins (indicating a high concentration), but UV–visible spectra of the same solutions indicated that only trace amounts were present.

Differences between the EXAFS and UV–visible results can be related to the microheterogeneous nature of asphaltene solutions and indicate that more than one quantitative method is needed to characterize metalloporphyrins in heavy fractions of petroleum oils. The microheterogeneity of each asphaltene solution must also be examined in detail. In this regard, the most accurate method involves SAXS (small-angle X-ray scattering),[10–14] which gives an average size of the scattering particles in solution. SAXS requires the use of model compounds to determine the absolute size of aggregates in the asphaltene sample. The utilized model compound should contain a macrocyclic unit and should also form micelles in solution. The most ideal model compound would be a micellar metalloporphyrin.

A number of porphyrins and metalloporphyrins are known to aggregate in aqueous solutions,[15,16] organic solvents,[17] or mixed

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(1) (a) University of Dijon. (b) University of Houston. (c) On leave from the University of Thessaloniki. (d) Societe Elf France.

(2) Barwise, A. J. G.; Whitehead, E. V. Symposium on Novel Methods of Metal and Heteroatom Removal. Presented at the 179th National Meeting of the American Chemical Society, Houston, TX, March 23–28, 1980.

(3) Fish, R. H.; Komlenic, J. J. *Anal. Chem.* **1984**, *56*, 510.

(4) Fookes, C. J. R. *J. Chem. Soc., Chem. Commun.* **1983**, 1472.

(5) Fookes, C. J. R. *J. Chem. Soc., Chem. Commun.* **1985**, 706.

(6) Ocampo, R.; Callot, H. J.; Albrecht, P. *J. Chem. Soc., Chem. Commun.* **1985**, 198.

(7) Reynolds, J. G.; Biggs, W. R.; Fetzer, J. C.; Gallegos, E. J.; Fish, R. H.; Komlenic, J. J.; Wines, B. K. *Collect. Colloq. Semin.* **1984**.

(8) Dickson, F. E.; Kunesh, C. J.; McGinnis, E. L.; Petrakis, L. *Anal. Chem.* **1972**, *44*, 978.

(9) Spencer, W. A.; Galobardes, J. F.; Curtis, M. A.; Rogers, L. B. *Sep. Sci. Technol.* **1982**, *17*, 797.

(10) Goulon, J. F.; Retournard, A.; Friant, P.; Goulon-Ginet, C.; Berthe, C.; Muller, J. F.; Poncet, J. L.; Guilard, R.; Escalier, J. C.; Neff, B. *J. Chem. Soc., Dalton Trans.* **1984**, 1095.

(11) Dickie, J. P.; Yen, T. F. *Anal. Chem.* **1967**, *39*, 1847.

(12) Pollack, S. S.; Yen, T. F. *Anal. Chem.* **1970**, *42*, 623.

(13) Kim, H.; Long, R. B. *Ind. Eng. Chem. Fundam.* **1979**, *18*, 60.

(14) Ho, B.; Briggs, D. E. *Colloids Surf.* **1982**, *4*, 285.

(15) (a) Takami, A.; Mataga, N. *J. Phys. Chem.* **1987**, *4*, 285. (b) White, W. I. In *The Porphyrins*; Dolphin, E., Ed.; Academic Press: New York, 1978; Vol. 5, Chapter 7. (c) Satterlee, J. D.; Shellnutt, J. A. *J. Phys. Chem.* **1984**, *88*, 5487. (d) Chadrashekar, T. K.; van Willigen, H.; Ebersole, M. H. *J. Phys. Chem.* **1984**, *88*, 4326. (e) Pasternack, R. F.; Gibbs, E.; Gaudemer, A.; Antebi, A.; Bassner, S.; DePoy, L.; Turner, D. H.; Williams, A.; Laplace, F.; Lansard, M. H.; Merriene, C.; Perree-Fauvet, M. *J. Am. Chem. Soc.* **1985**, *107*, 8179. (f) Kano, K.; Miyake, T.; Uomoto, K.; Sato, T.; Ogawa, T.; Hashimoto, S. *Chem. Lett.* **1983**, 1867. (g) Kano, K.; Nakajima, T.; Takei, M.; Hashimoto S. *Bull Chem. Soc. Jpn.* **1987**, *60*, 1281.

(16) Fuhrhop, J.-H.; Baccouche, M. *Liebigs Ann. Chem.* **1976**, 2058.

(17) Yamamura, T. *Chem. Lett.* **1977**, 773.

0020-1669/91/1330-1898$02.50/0