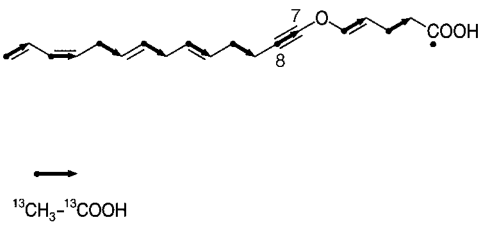


Figure 1. Biogenesis of maracin **1** from [1,2-$^{13}C_2$]acetate. The ^{13}C-labeled C_2 unit is represented by an arrow (blunt end: methyl C-atom, point: carboxy C-atom).

Artemisia lactiflora,[15] is, like **1**, also an ethynyl *trans*-vinyl ether. α-Chloro divinyl ethers were previously unknown as natural products.

According to initial results, maracin and maracen are active in vitro against the pathogen responsible for tuberculosis ($IC_{99} < 12.5\ \mu g\,mL^{-1}$);[16] whether they are also active in vivo has still to be demonstrated. With an in vitro toxicity of $\geq 24\ \mu g\,mL^{-1}$ against the mouse fibroblast line L929, they are supposedly of low toxicity for higher organisms and thus are possibly suitable for medical application.

Received on 12 November 1997 [Z11152IE]
German version: *Angew. Chem.* **1998**, *110*, 1313–1315

Keywords: antibiotics · myxobacteria · natural products · structure elucidation · vinyl ethers

---

[1] G. Rasch, *Bundesgesundheitsblatt* **1996**, *9*, 347–352.

[2] *Tuberculosis–Pathogenesis, Protection, and Control* (Ed.: B. R. Bloom), ASM Press, Washington, DC, **1994**; P. Scheinert, *Biotec* **1997**, *1*, 48–50.

[3] T. P. Gillis, R. C. Hastings in *Encyclopedia of Microbiology, Vol. 2* (Ed.: J. Lederberg), Academic Press, New York, **1992**, p. 601–610.

[4] C. M. Nolan, *J. Infect. Dis.* **1997**, *176*, 748–751.

[5] The trivial names maracin and maracen were derived from Massai Mara (Kenya), the place where the strain So ce880 was discovered.

[6] In addition to the main components, the following side products were isolated: So ce880: maracin B (95 mg, 19,20-dihydro derivative of **1**), maracin C (15 mg, (17*Z*) isomer of **1**), maracin D (20 mg, (17*Z*) isomer of maracin B), maracin E (3 mg, (4*Z*) isomer of maracin B); So ce1128: maracen B (186 mg, 19,20-dihydro derivative of **2**), maracen C (66 mg, (17*Z*) isomer of **2**), maracen D (62 mg, (17*Z*) isomer of maracen B).

[7] The coupling constant $J_{4\text{-H},5\text{-H}}$ is 5.7 Hz for the *cis*-vinyl ether (maracin E)[6].

[8] a) Compare with the value of 216.5 Hz in ethoxyacetylene: see ref. [8c], p. 151; b) (7*Z*)-**2**: δ(8-H) = 5.23 (calc.; ref. [8c], p. 118), 5.14 (det.); (7*E*)-**2**: δ(8-H) = 4.88 (calc.; ref. [8c], p. 118), 5.02 (det.); c) M. Hesse, H. Meier, B. Zeeh, *Spektroskopische Methoden in der organischen Chemie*, 4th ed, Thieme, Stuttgart, **1991**.

[9] Reaction of **1** with LiCl (excess) in acetic acid for 3 h at room temperature gave a mixture of (7*E*)-**2** and (7*Z*)-**2** with a yield of 35%.

[10] Compare P. J. Stang, V. V. Zhdankin in *Supplement C2: The Chemistry of Triple-bonded Functional Groups* (Ed.: S. Patai), Wiley, New York, **1994**, p. 1146–1147; reaction of **2** with lithium diisopropylamide in THF for 30 min at 0 °C gave **1** with 20% yield.

[11] **3** (only data differing from **1**): IR (KBr): $\tilde{\nu} = 1749, 1711, 1676, 1150\ cm^{-1}$; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 5.41$ (overlapping, 1H, 4-H), 7.12 (d, $J = 12.4$ Hz, 1H, 5-H), 2.39 (overlapping, 2H, 8-H), 1.70 (quint., $J = 7.2$ Hz, 2H, 9-H), 2.08 (q, $J = 7.2$ Hz, 2H, 10-H); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 112.8$ (C-4), 136.5 (C-5), 170.9 (C-7), 33.4 (C-8), 24.5 (C-9), 26.4 (C-10); DCI-MS (NH_3): $m/z = 317.1715$ (calc. for $[M - H]^-$: 317.1753).

[12] J. Nieuwenhuis, J. F. Arens, *Recl. Trav. Chim. Pays-Bas* **1958**, *77*, 1153.

[13] T. Galliard, D. R. Phillips, *Biochem. J.* **1972**, *129*, 743–753; L. Crombie, D. O. Morgan, E. H. Smith, *J. Chem. Soc. Perkin Trans. 1* **1991**, 567–575; Z.-D. Jiang, W. H. Gerwick, *Lipids* **1997**, *32*, 231–235.

[14] H. Hock, S. Lang, *Ber. Dtsch. Chem. Ges.* **1944**, *77*, 257.

[15] C. Xu, X. Sun, J. Yang, D. Yu, Q. Li, Y. Zhang, S. Dou, *Yaoxue Xuebao* **1986**, *21*, 772 [*Chem. Abstr.* **1986**, *106*, 135232e].

[16] Tuberculosis Antimicrobial Acquisition & Coordinating Facility of the National Institute of Allergy and Infectious Diseases, Birmingham, AL, USA; in this test, rifampicin had a IC_{98} value of $0.25\ \mu g\,mL^{-1}$.

π-Stacked *ortho*-Palladated Bipyridine Complexes Exhibiting Unusual Liquid Crystalline Behavior**

Abdelkrim El-ghayoury, Laurent Douce,
Antoine Skoulios, and Raymond Ziessel*

Liquid crystals (LCs) have many important applications, for example in the manufacture of visual display units or temperature sensors. Despite extensive and elegant investigations of their morphological properties, it is still hazardous to predict their precise structural behavior. Several major classes of LCs have been identified, such as nematic, smectic, and columnar, and crude guidelines have been established to specify the molecular requisites for LC properties. The design of an efficacious LC requires careful consideration of the molecular architecture that might induce the formation of the desired LC and, in some cases, also the prediction of molecular interactions in the emerging mesophase. In fact, mesomorphic materials provide some of the best examples of intermolecular interaction or self-assembly at the supramolecular level.

In the search for new LCs, metal-containing mesogens (metallomesogens) have recently attracted considerable attention owing to the possibility of combining the properties of the metal (color, magnetism, polarizability, redox behavior, electronic charge, resistivity, etc.) with those of the organic framework.[1, 2] Such substances have tremendous potential as

---

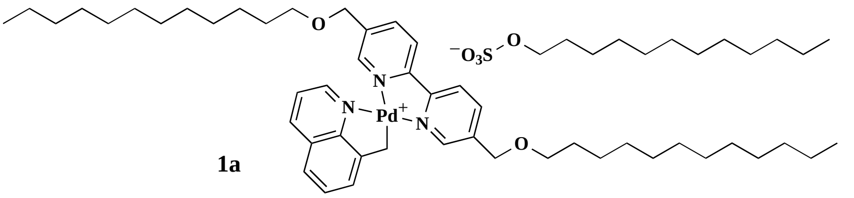
[*] Dr. R. Ziessel, A. El-ghayoury, Dr. L. Douce
Laboratoire de Chimie, d'Electronique et de
Photonique Moléculaires
Ecole Chimie, Polymères, Matériaux (ECPM)
UPRES-A 7008 au CNRS, 1 rue Blaise Pascal
F-67008 Strasbourg Cedex (France)
Fax: (+33) 388-416-825
E-mail: ziessel@chimie.u-strasbg.fr
Dr. A. Skoulios
Groupe des Matériaux Organiques
Institut de Physique et Chimie des Matériaux
UMR 46 au CNRS, 23 rue du Loess
F-67037 Strasbourg Cedex (France)

[**] We warmly thank Prof. Anthony Harriman for fruitful discussions, Prof. Robert Deschenaux for the DSC measurements, and Prof. Duncan Bruce for helpful advice concerning preparation of the silver salts. This work was partially supported by the Ecole Chimie, Polymères, Matériaux (ECPM) and the Centre National de la Recherche Scientifique.

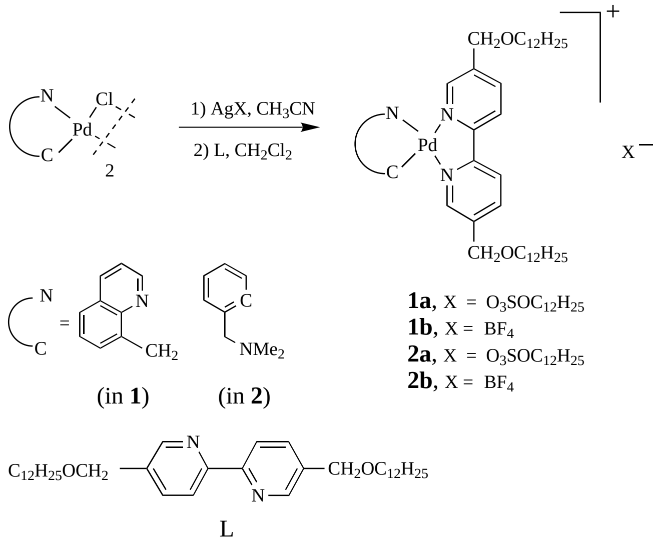
low molecular-mass systems addressable by weak magnetic or optical fields. In particular, *ortho*-palladated mono[3] and dinuclear complexes, which yielded the first ferroelectric[4] and cholesteric organometallic mesogens,[5] form a major cornerstone of the subject.

Recently, considerable effort has been expended on the development of new thermotropic bipyridine-based (bipy) molecules in order to combine the powerful chelating properties of bipy with the proven self-organizational ability of the ancillary aliphatic chains.[6, 7] Surprisingly, only one example of a bipyridine-based metallomesogen has been reported so far. The rodlike molecule contains four phenyl rings in addition to the aryl ligands that form the primary coordination shell.[8, 9] In contrast to this calamitic (rodlike) approach we suggest the use of transition metal complexes displaying discotic (disklike) structure.

We now report that direct attachment of two dodecyl chains to the bipy chelator through an ether linkage leads to a nonmesogenic material. Subsequent coordination of a cyclopalladated fragment gives rise to a hitherto unreported family of cationic complexes, some of which display LC behavior. Interestingly, the poor thermal stability of the tetrafluoroborate salt **1b** is eradicated by the use of an alkylsulfate counteranion **1a**.


1a

Cyclopalladated complexes **1a**, **1b**, **2a**, and **2b** were prepared by the adaptation of a literature method based on 2-phenylpyrimidine (Scheme 1).[10] The nonmesogenic bipyridine ligand L was obtained by nucleophilic substitution of 5,5′-di(bromomethyl)-2,2′-bipyridine[11] with sodium *n*-dodecyl alcoholate (yield 70 %). The required palladium-containing fragment was obtained by silver dehalogenation of the [Pd(8-mq)Cl]$_2$[12] (8-mq = 8-methylquinoline) or [Pd(dmba)Cl]$_2$[13] (dmba = *o*-(N,N-dimethylaminomethyl)phenyl) dimers. Subsequent reaction with L gave the desired pale yellow complexes **1a**, **1b**, **2a**, and **2b** in high yield, which have been unequivocally characterized by ^{1}H and ^{13}C{^{1}H} NMR, FT-IR, and UV/Vis spectroscopy, FAB-MS, and elemental analysis.



Scheme 1. Synthesis of the palladium complexes **1a**, **1b**, **2a**, and **2b**.

Initial examination of the complexes with polarizing optical microscopy, differential scanning calorimetry (DSC), and X-ray diffraction showed that **2a** and **2b** melt upon heating directly into an isotropic liquid (probably because steric hindrance of the geminal methyl groups perturb the flatness of the aromatic cores). In contrast, **1a** and **1b** are perfectly able, as expected, to produce thermotropic LCs. The complex salt **1b** degrades quickly when heated at high temperature, while **1a** is fairly stable, resisting a two-hour heat treatment at 185°C without detectable damage. In the present work, attention was thus focused on the liquid crystal behavior of **1a** only.

The DSC thermograms of **1a**, in the temperature range from 25 to 220°C, displayed two sharp peaks at 131 and 168°C, indicative of reversible first-order transitions. The optical textures observed upon slow cooling from the isotropic melt showed the emergence of a smectic *A* phase at 216°C (appearance of Bâtonnet textures, turning into focal conic, then into homeotropic) and of one other liquid crystal phase at 168°C, which resembled a smectic *C* phase (appearance of fine Schlieren textures) but was, in fact, columnar in symmetry as shown by X-ray diffraction.

$$\text{crystal} \xleftrightarrow[11.8\,\text{J g}^{-1}]{131\,^\circ\text{C}} \text{columnar} \xleftrightarrow[2.7\,\text{J g}^{-1}]{168\,^\circ\text{C}} \text{smectic A} \xleftrightarrow[5.7\,\text{J g}^{-1}]{216\,^\circ\text{C}} \text{isotropic liquid}$$

The X-ray diffraction pattern of the crystal contains several Bragg reflections consistent with a (pseudo)orthorhombic crystal lattice: $a = 12.67$, $b = 3.53$, $c = 33.60$ Å. The *b* period coincides with the known stacking separation of polynuclear aromatic molecules,[14] suggesting that the aromatic cores of the molecules[15] are stacked on top of one another to form columns aligned along the *b* axis of the crystal. The *a* period correlates with the lateral dimensions of the aromatic cores, suggesting that the columns lie side by side in close contact with one another, to form well-defined layers. The existence of several (00*l*) reflections shows that the aromatic layers are stacked along the *c* axis to form a lamellar crystal. The *c* period is larger than the size of the aromatic cores and smaller than the overall length (44.4 Å) of the molecules in a fully extended conformation; the molecules must therefore be arranged in single layers in which the flat aromatic cores lie parallel to the *b*,*c* crystal faces and the alkyl chains are tilted with respect to the layer normal. The dodecylsulfate counterions are inserted among the alkyl chains of the bipyridine moieties inside the aliphatic sublayers, with their ionic headgroups as close as possible to the positively charged palladium centers (vide supra).

The X-ray pattern of the columnar phase (Figure 1) contains a diffuse band (*A*, Figure 1) at 4.6 Å which shows that the alkyl chains have a liquidlike structure and are

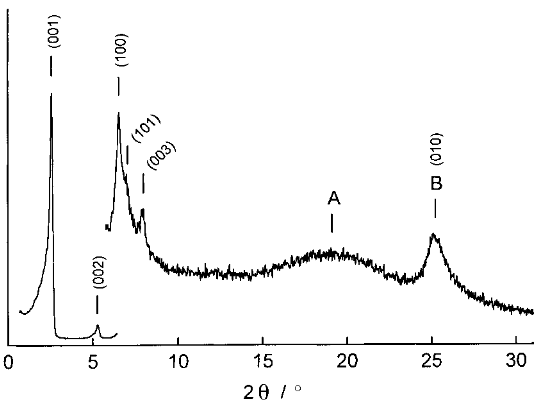


Figure 1. X-ray diffraction pattern of the columnar phase of **1a** at 152°C. For clarity, the intensities of the peaks at Bragg angles $2\theta > 5^\circ$ have been multiplied by 15. Numerals are Miller indices of the reflections (defined by the pseudo-orthorhombic lattice parameters a, b, c of the crystalline phase).

segregated from the aromatic cores. A broad band (*B*, Figure 1) at 3.53 Å indicates that the aromatic cores are stacked together to form columns, as in the crystal but in a looser fashion (with a correlation length of 65 Å, estimated from the width of the band). Five sharp reflections in the small-angle region are consistent with a two-dimensional rectangular lattice: $a = 13.5$, $c = 33.4$ Å, which is almost identical with the a,c lattice dimensions of the crystal (the small expansion of the a period suggests an "unlocking" of the columns inside the layers, consistent with the observed loosening of the intracolumnar stacking of the aromatic cores). It thus appears that the structure of the columnar phase is very similar to that of the crystal: the aromatic cores are stacked in columns; these lie side by side in close contact with one another to form well-defined layers, and the layers, separated by the disordered alkyl chains, stack to form a periodic lamellar structure (Figure 2). The absence of general (hkl) reflections suggests that the layers (or columns) are gliding freely along the columnar axis while maintaining position in the perpendicular direction. From the cell parameters, it is apparent that the aromatic cores cover an area of $13.5 \times 3.53 = 47.7$ Å^2 in the a,c plane, allowing the molten alkyl chains (including those of the alkylsulfate anions) a reasonable cross-sectional area of $2 \times 47.65/3 \approx 31.8$ Å^2.

The diffraction pattern of the smectic *A* phase contains, as expected, a diffuse band at 4.6 Å, characteristic of the disordered conformation of the alkyl chains, together with two sharp reflections in the small-angle region, related to a smectic single-layer arrangement of the molecules with a period of 31.3 Å. But in addition, they contain two diffuse bands at the same spacings as the sharp (100) and (010) reflections of the columnar phase, which reveal a local ordering of the molecules inside the layers reminiscent of the structure of the columnar phase. This structure is similar to that reported by Levelut et al.[16] for the smectic *A* phase of a conducting charge-transfer assembly of tetrathiofulvalene and tetracyanoquinodimethane, in which the aromatic cores of the molecules have a tendency to stack to form juxtaposed short columns randomly oriented inside the smectic layers.

Although complying rigorously with the symmetry requirements of columnar LCs (the long-range positional ordering of the molecules is fully described by a two-dimensional crystal lattice), the columnar phase discussed in the present work is none the less quite unusual. Breaking the general rule, the columnar cores are not surrounded by the molten alkyl chains and thus entirely isolated from one another, but are joined together to form well-defined compact layers that are separated by the alkyl chains and stacked periodically. From a purely phenomenological point of view, one might wonder, therefore, whether the columnar phase could not be equally well described as a smectic mesophase, or more precisely, as an ordered smectic phase with one-dimensional ordering of the molecules within the layers. Such a phase would be a type of plastic mesophase, because the interactions between the columns are stronger than across the layers, so that the aromatic layers are able to slip on top of each other under moderate shear stresses in a direction normal to the columnar axis.

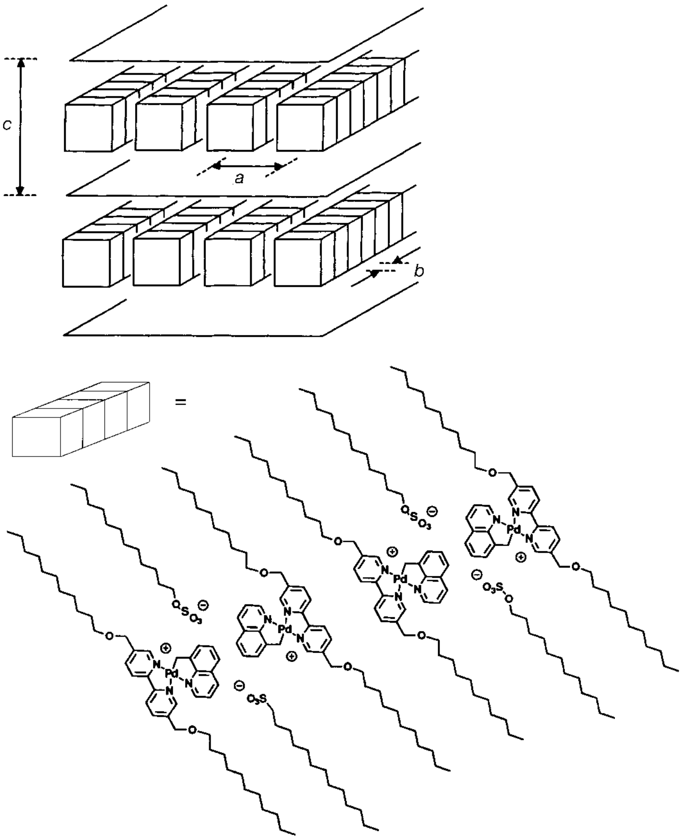


Figure 2. Idealized schematic view of the molecular packing of **1a**. The flat molecular cores of Pd atoms and coordinated aromatics rings (represented as boxes) are stacked on top of each other along the b direction to form columns (bottom half); these columns are juxtaposed along the a direction to form layers; and the layers stack along the c direction to form a lamellar structure.

In summary, we have developed a novel synthetic strategy using the coordination of *ortho*-palladated quinolines with nonmesogenic alkyl-disubstituted 2,2′-bipyridine residues. By reducing the number of phenyl rings in the complexes to a minimum, we were able to obtain LCs at relatively low temperatures, and thus avoid thermal degradation. By studying these new complexes with X-ray diffraction, we were able to identify a smectic *A* and a columnar liquid crystalline phase, both of which contained flat aromatic cores stacked on top of each other to form columns. The columns were arranged in compact layers separated by the alkyl chains in a disordered conformation. Obviously, these special structures are a result of stereochemical demands of the cation, the stacking ability of the ancillary *ortho*-palladated ligand, and the insertion of the counteranion among the alkyl chains. The packing mode of the aromatic cores may be optimized depending on the position of the alkyl chains on the bipy residues. The lamellar morphology of the columnar phase indicates that macroscopically oriented samples could be easily produced and could be profitably exploited for their physical properties. Because columns of closely stacked aromatic units are accessible at modest temperatures, we anticipate that these materials could be used as medium-length molecular wires or chemical sensors.

Experimental Section

L: Dodecanol (ca. 2 g) was heated with Na (0.08 g) for 2 h at 80°C to yield a white precipitate of $C_{12}H_{25}ONa$. After cooling to 20°C, a suspension of 5,5′-dibromomethyl-2,2′-bipyridine (0.30 g, 0.94 mmol) in anhydrous THF (5 mL) was added dropwise. The mixture was heated under reflux for 24 h. After distillation of the solvent, the residue was purified over a chromatography column (flash silica, *n*-hexane/CH_2Cl_2, gradient of 1/1 to 0/1). The analytically pure ligand L was then obtained (0.36 g, 70%). R_f = 0.65, SiO_2, CH_2Cl_2/MeOH: 98/2; m.p. 60–62°C; UV/Vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$: 290 nm (28500); ^1H NMR (200.1 MHz, $CDCl_3$, 25°C): $\delta = 8.6$ (s, 1H; H^6), 8.4 (d, $^3J = 8$ Hz, 1H; H^3), 7.8 (dd, $^3J = 8$ Hz, $^4J = 2$ Hz, 1H; H^4), 4.6 (s, 2H; bipy-CH_2), 3.5 (t, $^3J = 6$ Hz, 2H; OCH_2), 1.6 (m, 2H; OCH_2CH_2), 1.3 (broad s, 18H; $(CH_2)_9$), 0.9 (t, $^3J = 6$ Hz, 3H; CH_3); $^{13}C\{^1H\}$ NMR (50.1 MHz, $CDCl_3$, 25°C): $\delta = 154.7–120.1$ (aromatic C), 70.2 (bipyCH_2), 69.6 (OCH_2), 31.3 (OCH_2CH_2), 29.1 ($(CH_2)_3$), 28.9 (CH_2), 28.8 (CH_2), 28.7 (CH_2), 25.5 ($CH_3CH_2CH_2$), 22.1 (CH_3CH_2), 13.5 (CH_3); IR (KBr): $\tilde{\nu} = 2925$ (s), 2853 (s), 1598 (w), 1553 (w), 1467 (m), 1384 (w), 1350 (w), 1109 cm^{-1} (s). FAB^+-MS: *m*/*z* (%): 553.4 (100) $[M^+]$, 383.2 (32) $[M^+ - C_{12}H_{25}]$; elemental analysis calcd for $C_{36}H_{60}N_2O_2$ (552.465): C 78.21, H 10.94, N 5.07; found: C 78.09, H 10.79, N 5.02.

1a: A solution of $AgO_3SOC_{12}H_{25}$ (0.034 g, 0.090 mmol) in anhydrous CH_3CN (5 mL) was added at 20°C under argon, to a stirred suspension of $[Pd(8\text{-}mq)Cl]_2$ (0.026 g, 0.045 mmol). A white precipitate of AgCl appeared instantaneously. After 2 h, the solution was filtered over celite under argon. The filtrate was evaporated to dryness, and a solution of 5,5′-di(dodecyloxymethyl)-2,2′-bipyridine (0.05 g, 0.09 mmol) in anhydrous CH_2Cl_2 (5 mL) was added. The yellow solution was stirred for 2 h, and the product was precipitated by addition of pentane (10 mL). **1a** was recovered by centrifugation as a yellow powder (0.08 g, 84%). UV/Vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$: 229 nm (45500), 243 (43800), 315 (25900); ^1H NMR (200.1 MHz, $CDCl_3$, 25°C): $\delta = 9.1$ (d, 1H; aromatic H), 8.8 (s, 1H; aromatic H), 8.6 (dd, 2H; aromatic H), 8.4 (s, 1H; aromatic H), 8.2 (d, 1H; aromatic H), 8.1 (pseudo t, 2H; aromatic H), 7.9 (dd, 1H; aromatic H), 7.5 (m, 3H; aromatic H), 4.8 (s, 2H; bipy-CH_2), 4.5 (s, 2H; bipy-CH_2), 4.2 (t, $^3J = 7$ Hz, 2H; O_3SOCH_2), 3.75 (s, 2H; CH_2Pd), 3.6 (m, 4H; OCH_2), 1.7 (m, 6H; OCH_2CH_2), 1.3 (broad s, 54H; $(CH_2)_{27}$), 0.9 (t, $^3J = 6$ Hz, 9H; CH_3); $^{13}C\{^1H\}$ NMR (50.1 MHz, $CDCl_3$, 25°C): $\delta = 155.2–123.5$ (aromatic C), 71.6 (bipyCH_2), 69.0 (OCH_2), 67.6 (O_3SOCH_2), 34.4 (CH_2Pd), 32 (CH_2), 29.8 $[(CH_2)_n]$, 29.6 (CH_2), 29.4 (CH_2), 26.4 (CH_2), 26.2 (CH_2), 22.7 (CH_2), 14.2 (CH_3); IR (KBr): $\tilde{\nu} = 3055$ (w), 2923 (s), 2854 (s), 1604 (w), 1509 (w), 1468 (m), 1386 (w), 1251 (s), 1223 (s), 1117 cm^{-1} (s). FAB^+-MS: *m*/*z* (%): 800.4 (100) $[M - O_3SOC_{12}H_{25}]^+$, expected isotopic profile, 658.3 (8) $[M - O_3SOC_{12}H_{25} - mq]$, 630.2 (30) $[M - O_3SOC_{12}H_{25} - C_{12}H_{25}]$, 247.9 (45) $[M - O_3SOC_{12}H_{25} - L]$; elemental analysis calcd for $C_{58}H_{93}N_3O_6SPd$ (1065.58): C 65.32, H 8.80, N 3.94; found: C 65.17, H 8.61, N 3.69.

Received: November 4, 1997
Revised version: January 9, 1998 [Z11119IE]
German version: *Angew. Chem.* **1998**, *110*, 1303–1306

Keywords: bipyridine · metallomesogens · N ligands · palladium · stacking interactions

---

[1] A. P. Polishchuk, T. V. Timofeeva, *Russ. Chem. Rev.* **1993**, *62*, 291; D. W. Bruce in *Inorganic Materials*, 2nd ed. (Eds.: D. W. Bruce, D. O'Hare), Wiley, New York, **1996**, pp. 429–522; J. L. Serrano, T. Sierra in *Metallomesogens* (Ed.: J. L. Serrano), VCH, Weinheim, **1996**, pp. 43–129.

[2] R. Deschenaux and J. W. Goodby in *Ferrocenes* (Eds.: A. Togni, T. Hayashi), VCH, Weinheim, **1995**, chap. 9, pp. 471–495.

[3] N. J. Thompson, J. L. Serrano, M. J. Baeana, P. Espinet, *Chem. Eur. J.* **1996**, *2*, 214.

[4] P. Espinet, J. Etxebarria, M. Marcos, J. Pérez, A. Remon, J. L. Serrano, *Angew. Chem.* **1989**, *101*, 1076; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1065.

[5] M. J. Baena, J. Buey, P. Espinet, H.-S. Kitzerow, G. Heppke, *Angew. Chem.* **1993**, *105*, 1238; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1201.

[6] L. Douce, R. Ziessel, R. Seghrouchni, A. Skoulios, E. Campillos, R. Deschenaux, *Liq. Cryst.* **1995**, *18*, 157; *ibid.* **1996**, *20*, 235; A. El-ghayoury, L. Douce, R. Ziessel, R. Seghouchni, A. Skoulios, *ibid.* **1996**, *21*, 143.

[7] K. E. Rowe, D. W. Bruce, *Liq. Cryst.* **1996**, *20*, 183.

[8] K. E. Rowe, D. W. Bruce, *J. Chem. Soc. Dalton Trans.* **1996**, 3913.

[9] F. Neve, M. Ghedini, A. Crispini, *Chem. Commun.* **1996**, 2463.

[10] M. Ghedini, D. Pucci, *J. Organomet. Chem.* **1990**, *395*, 105.

[11] R. Ziessel, M. Hissler, G. Ulrich, *Synthesis* **1998**, in press.

[12] A. J. Deeming, I. P. Rothwell, *J. Organomet. Chem.* **1981**, *205*, 117.

[13] A. C. Cope, E. C. Friedrich, *J. Am. Chem. Soc.* **1968**, *90*, 909.

[14] A. I. Kitaigorodskii, *Organic Chemical Crystallography*, Consultants Bureau, New York, **1961**, p. 7.

[15] In fact, because of the steric repulsion between the *ortho*-hydrogen atoms of the palladated nitrogen atoms, the aromatic cores are not perfectly planar but slightly twisted.

[16] P. Davidson, A. M. Levelut, H. Strzelecka, V. Gionis, *J. Phys. Fr.* **1983**, *44*, L823.

Anion Control in the Self-Assembly of a Cage Coordination Complex[**]

Ramón Vilar, D. Michael P. Mingos,[*]
Andrew J. P. White, and David J. Williams

Anion binding and recognition has attracted increasing interest because of its importance in biological and chemical processes.[1, 2] Many enzyme reactions involve the selective transformation of anions.[1] The selective extraction of anionic pollutants also requires the development of specific coordination sites.[2a] Classically, cations have been used to promote the assembly of ligands,[3] but recently interest has been shown in using anions as templates for the formation of supramolecular entities.[4]

The supramolecular interactions required for anion-assisted self-assembly involve either Lewis acid–base interactions between a metal cation and an anion[5, 6] or hydrogen-bonding

---

[*] Prof. D. M. P. Mingos, Dr. R. Vilar, Dr. A. J. P. White,
Prof. D. J. Williams
Department of Chemistry, Imperial College
London SW7 2AY, (UK)
Fax: (+44) 171-594-5804
E-mail: d.mingos@ic.ac.uk

[**] We thank the Engineering and Physical Sciences Research Council for financial support and BP for the endowment of D.M.P.M.s chair.