Stereochemical Aspects of Metal-Containing Liquid Crystals (part II)

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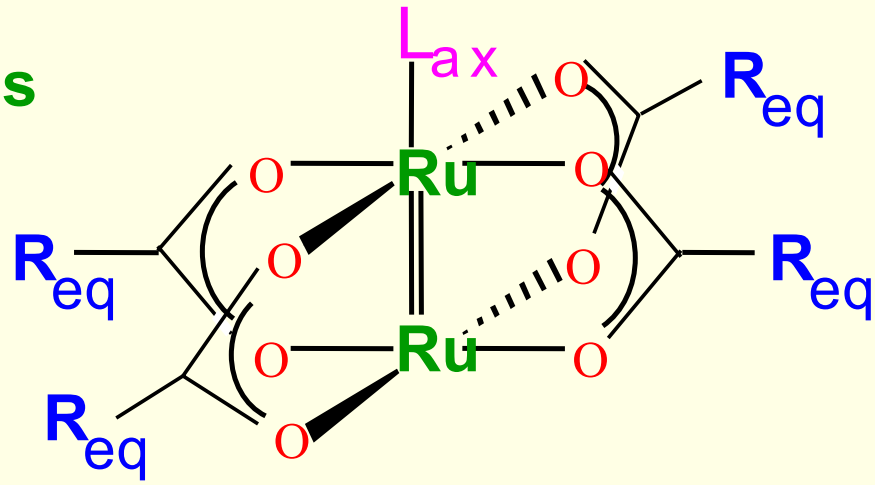
Selected examples showing the influence of molecular shape and volume (including chirality) on mesomorphic properties, mesophase structure and physical properties of metallomesogens

3rd example: Dirhutenium carboxylates: Molecular design of columnar LC order

Metal-Metal bonded systems

Building Blocks for Coordination Polymers



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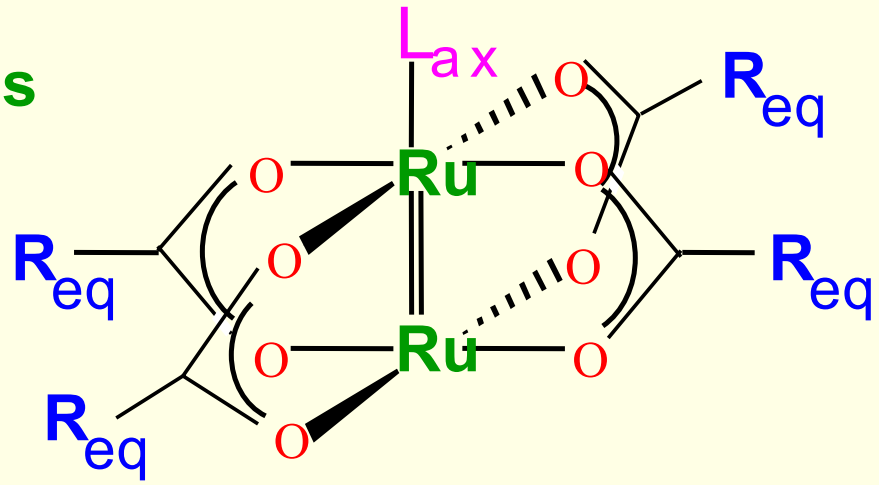


I – Molecular Structure / LC properties relationship

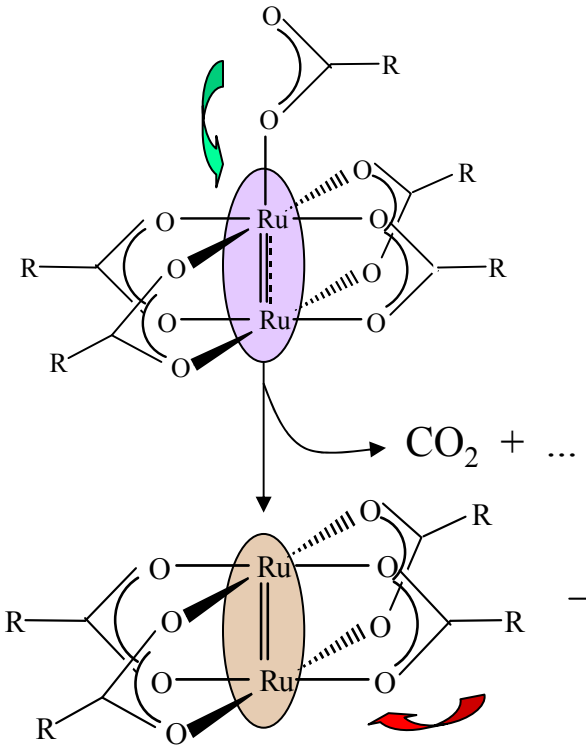
II – Model for the Lamellar Crystalline phase of $Ru_2(O_2CR)_4X$ series

III – A model for the Col_H mesophase of the $Ru_2(O_2CR)_5$ series

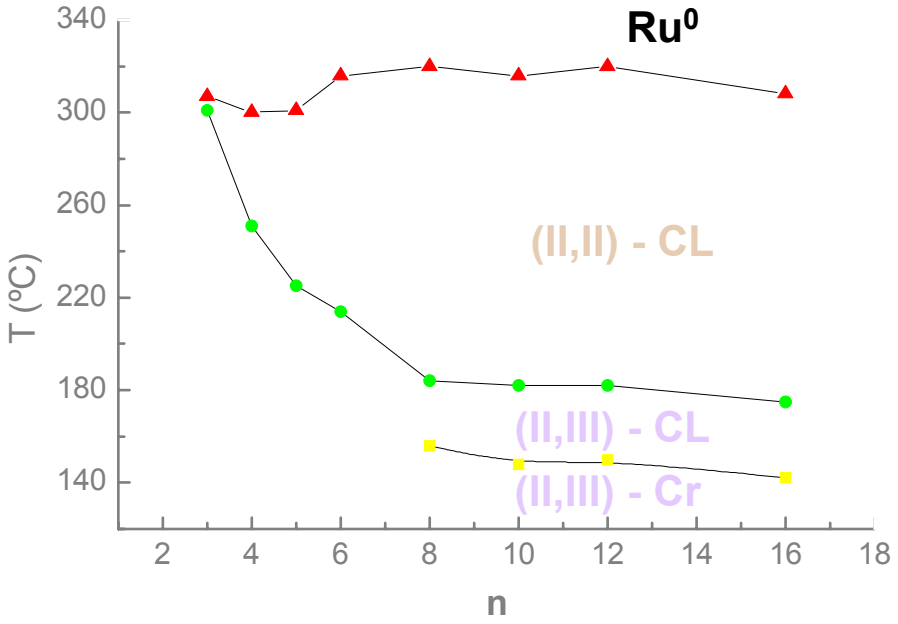
IV - Magnetic Properties of $Ru_2(O_2CR)_4X$

V – Thermal Decomposition / Stability

$Ru_2(O_2CR)_5$



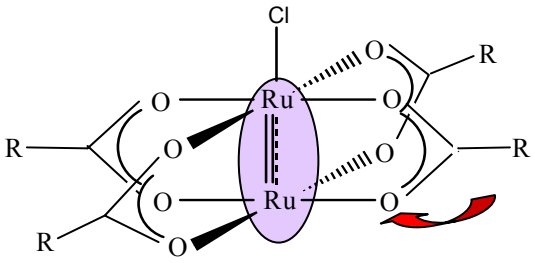
CO_2 + ...



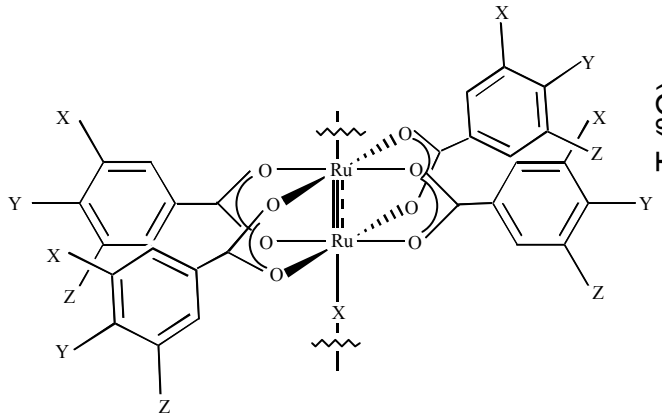
$Ru^0 + CO_2 + ...$

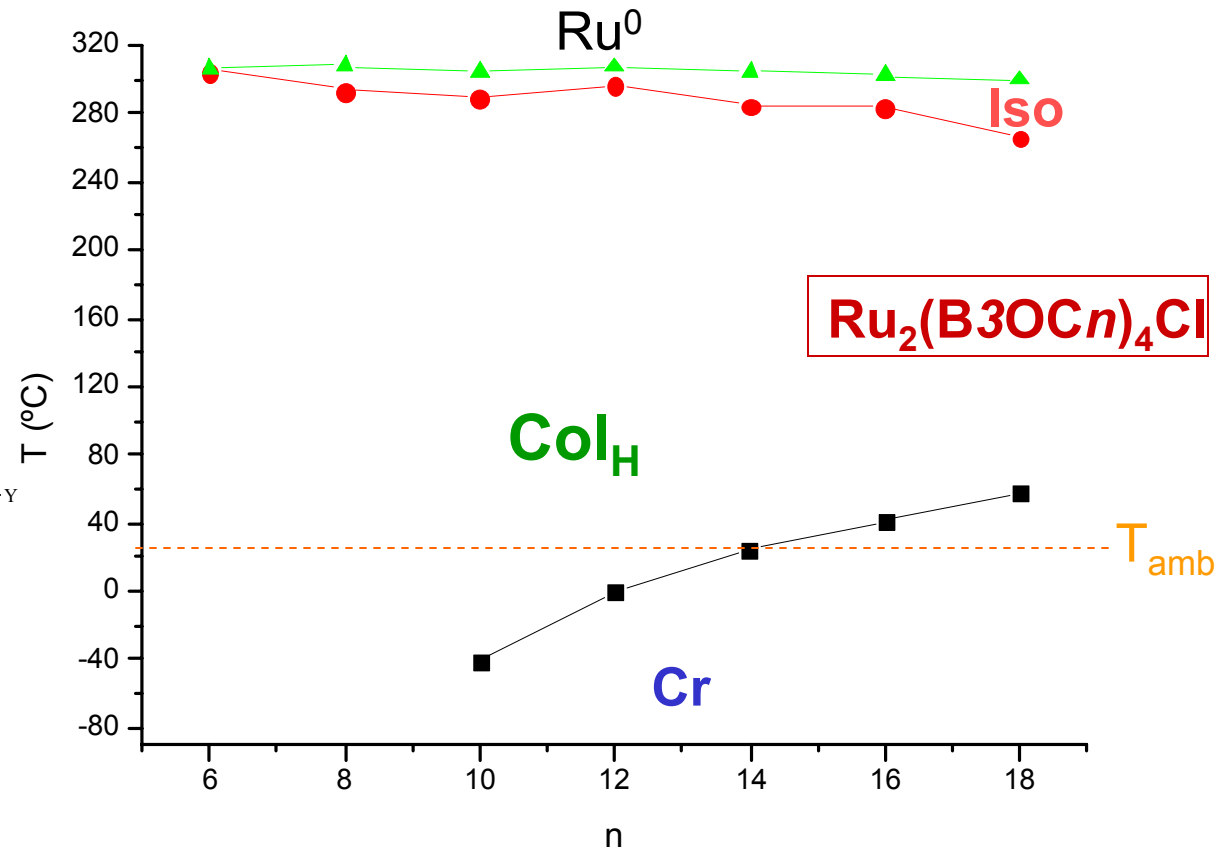
Rusjan *et al*, *Solid State Ionics* **124**, 143 (1999)

Stereoch. Asp. Metallomesogens – Ex. #3 (Stability of $Ru_2(O_2CR)_4X$)



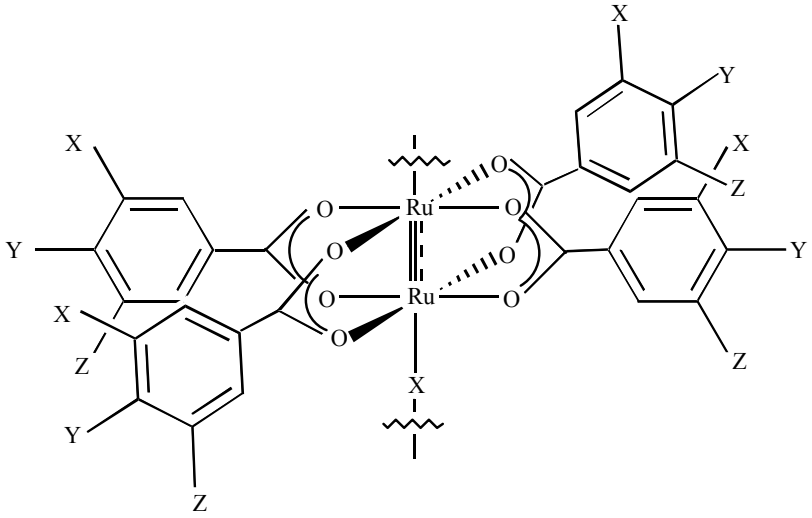
$$Ru^0 + CO_2 + \ldots$$

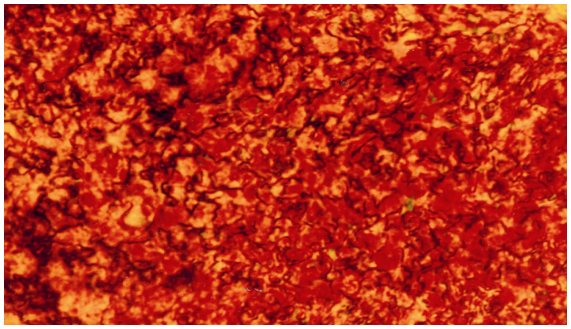


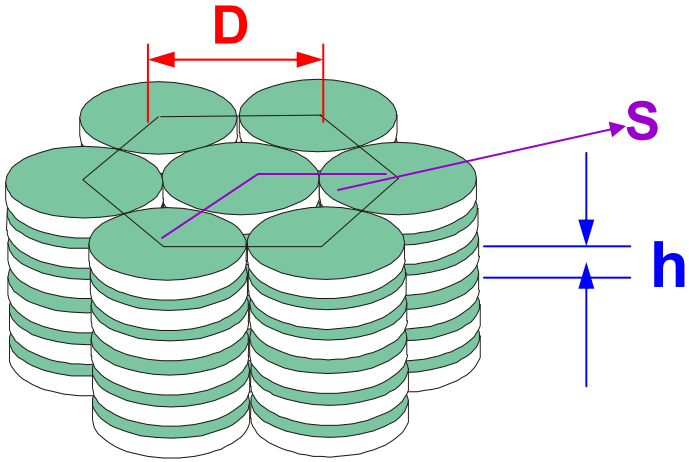


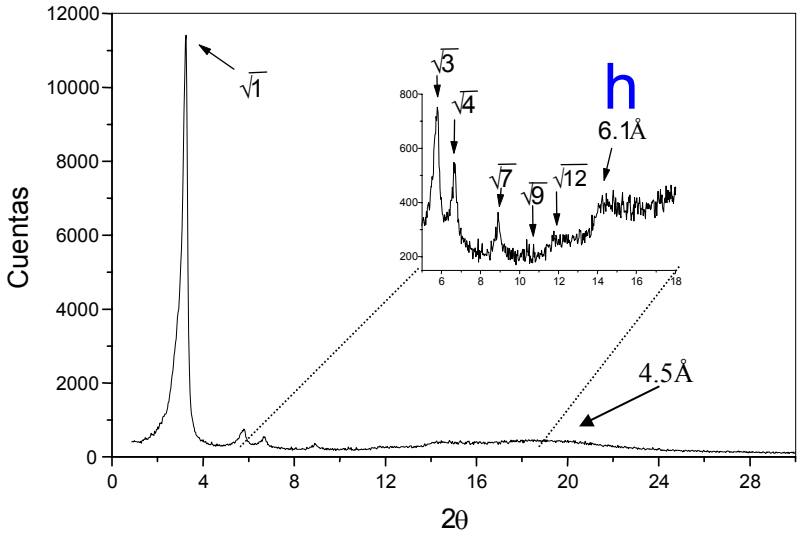
Rusjan *et al*, *Solid State Ionics* **159**, 389 (2003)

VI –Supramolecular Structure in Col_H $Ru_2(B3OCn)_4Cl$





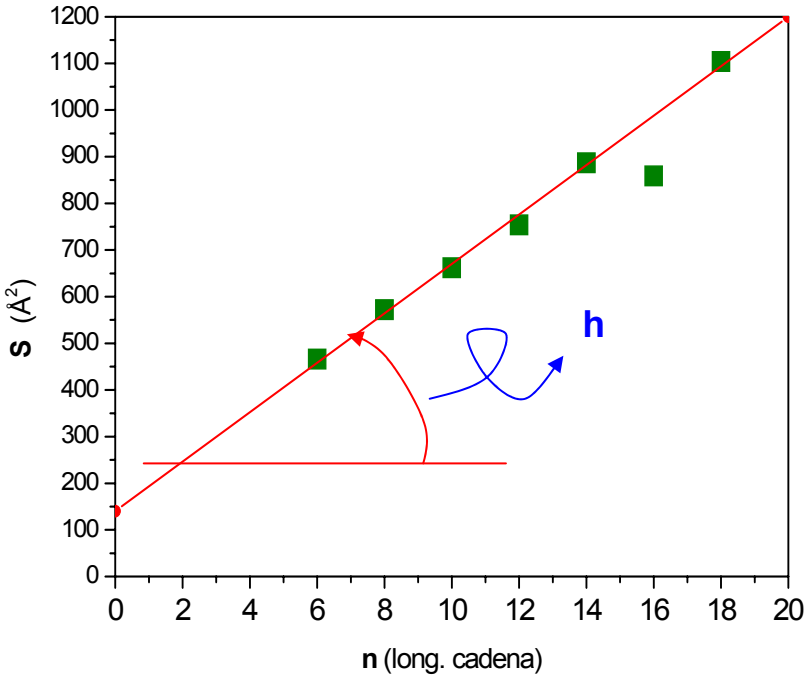




$Col_{H.O}$ at RT

Mesomorphic range ≈ 300ºC

Stereoch. Asp. Metallomesogens – Ex. #3 (Model for $Ru_2(B3OCn)_4Cl$)



$$h^{est} \cong Vo^{est} / S_{XRD}$$

$$Vo^{est} \cong V\ Ru_2(O_2CPh)_4Cl + 12\ ((n\text{-}1)\ VCH_2 + VOCH_3)$$

Checked against results from dilatometry and flotation experiments

$$V = S.h = p\ Vo$$

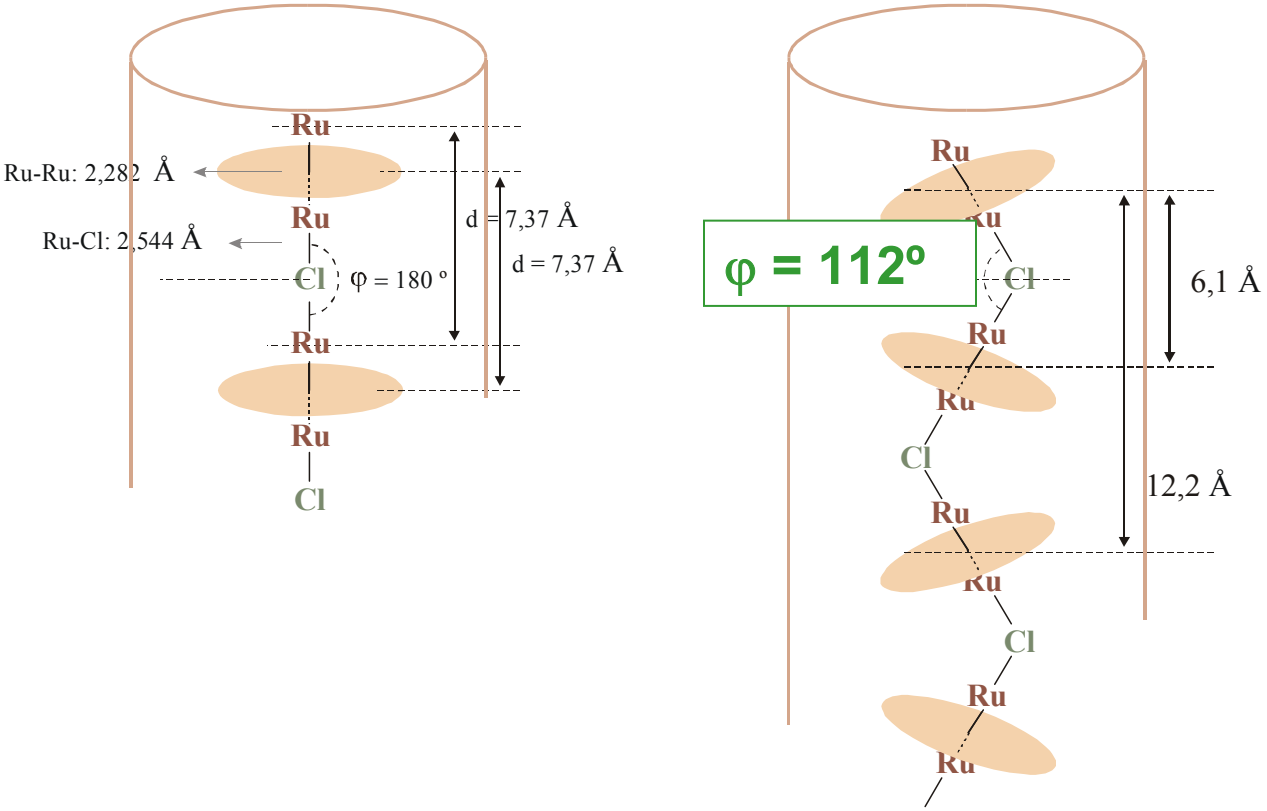
$$Vo = V_{pc} + 12\ (n\ VCH_2 + \Delta VCH_3)$$

$$S = (p/h)\ [V_{pc} + 12\ \Delta VCH_3] + (p/h)\ 12\ n\ VCH_2$$

3 independent estimations for $h \approx 6.1 – 6.4$ Å

3 independent estimations for **h ≈ 6.1 – 6.4 Å < 7.4 Å** (Σd)

What are the molecular and supramolecular structures giving rise to this Col_H mesophase?



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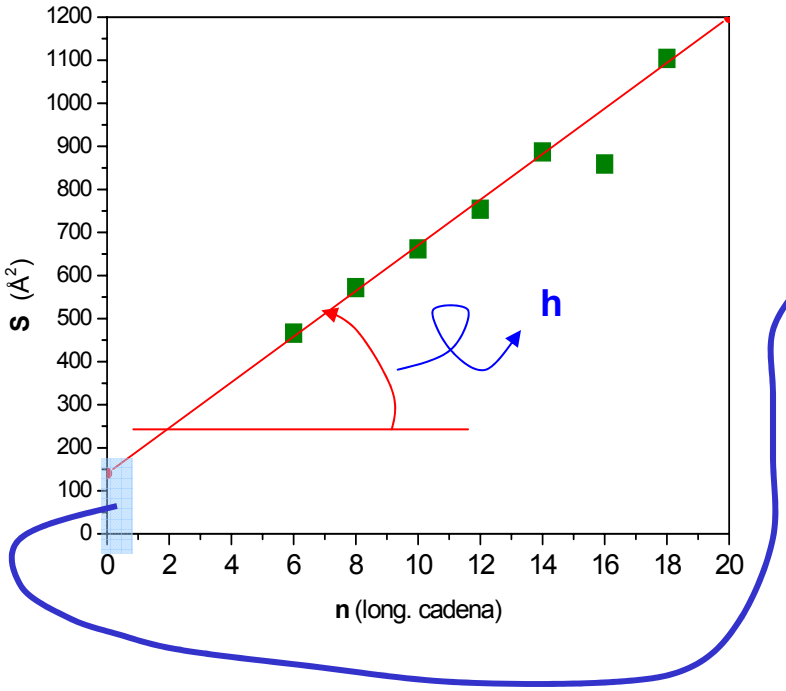
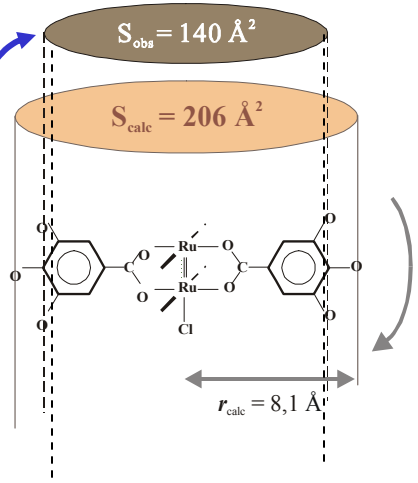
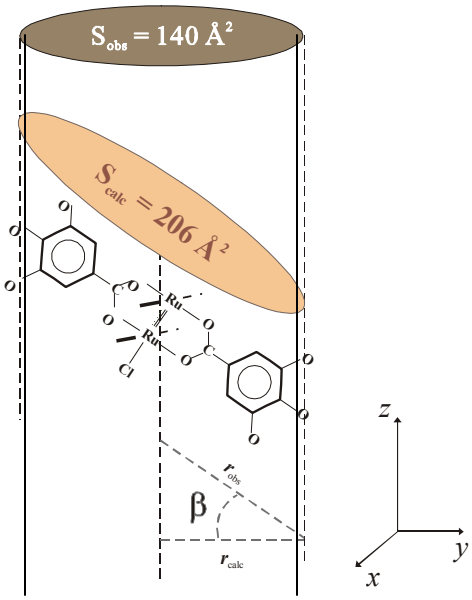
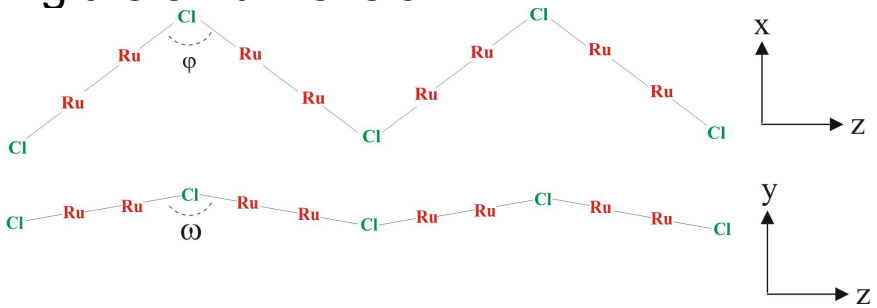






$$\cos^2 \beta = r_{obs}^2/r_{calc}^2 \quad \Rightarrow \quad \beta = 34^o$$

In fact, including the 3rd dimension:



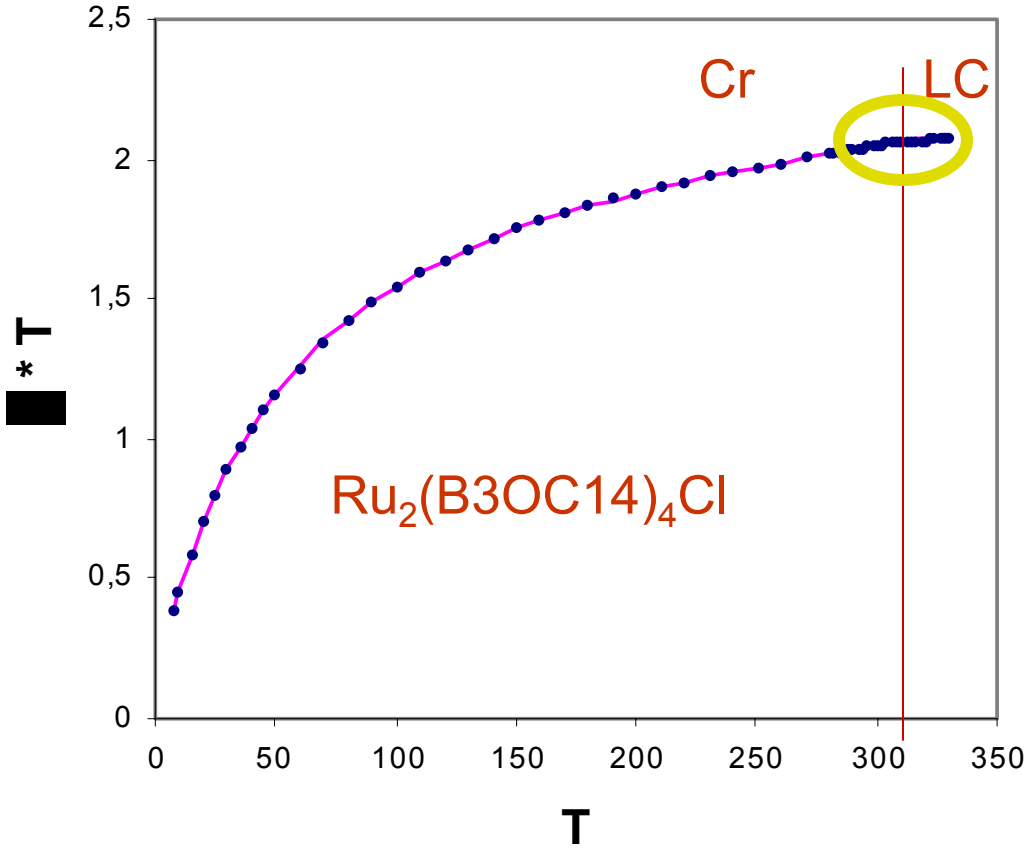
complement of 112°/2 !

Constraints on φ and h can be reduced

Is the molecular binuclear structure preserved in Col_H?

LOCAL PROBES:

1) Molecular Magnetism (SQUID)



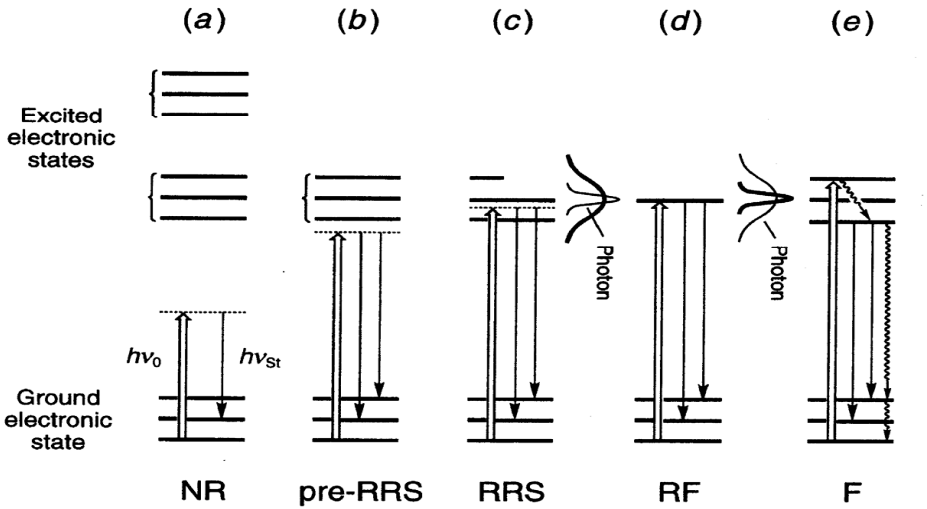
S = 3/2, ZFS + zJ

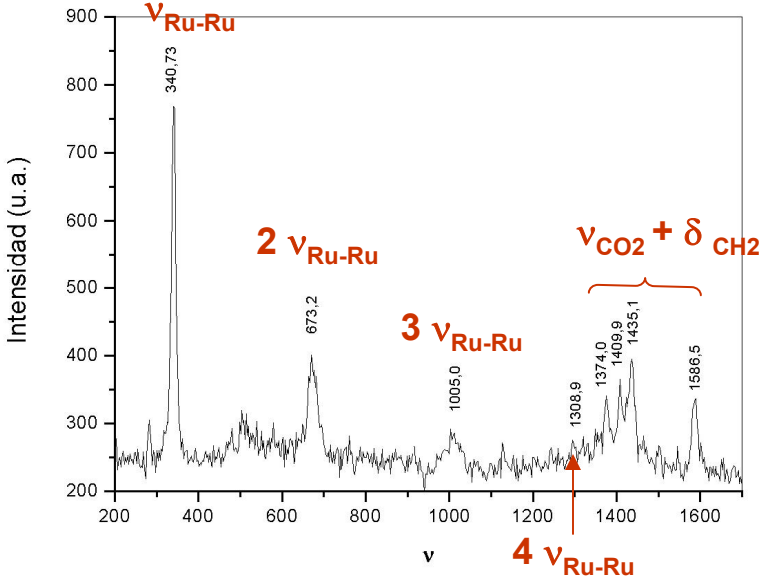
D = 56 cm^{-1}

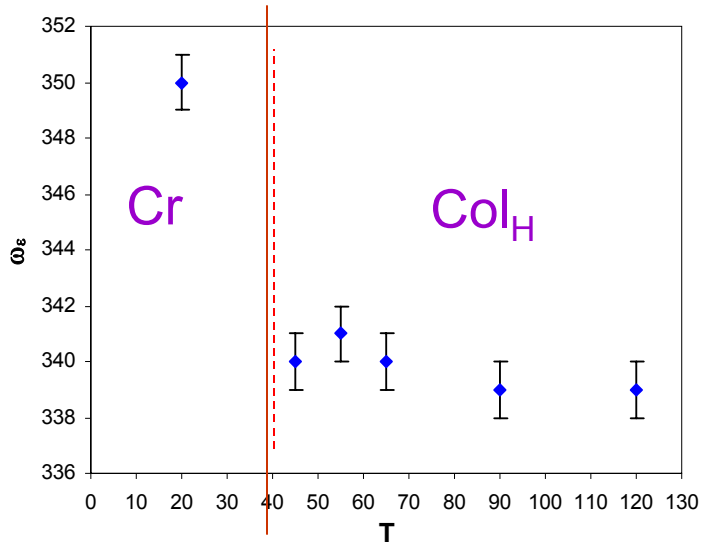
zJ = - 8 cm^{-1}

LOCAL PROBES:

2) Resonance Raman

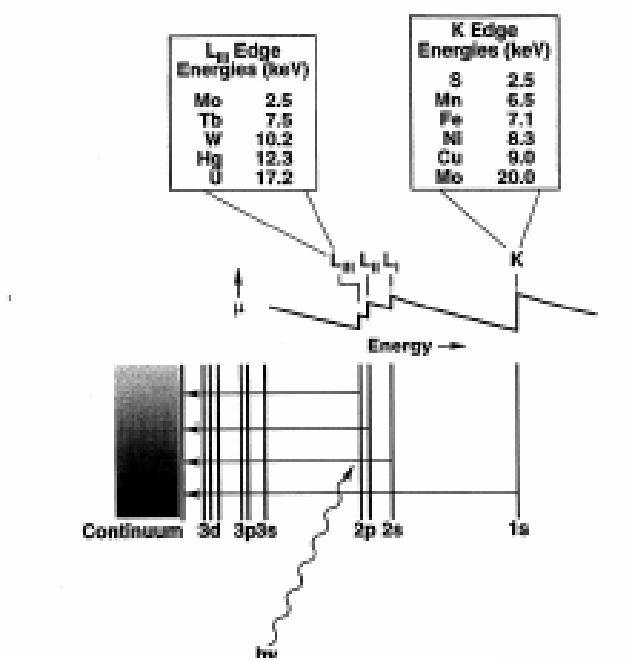


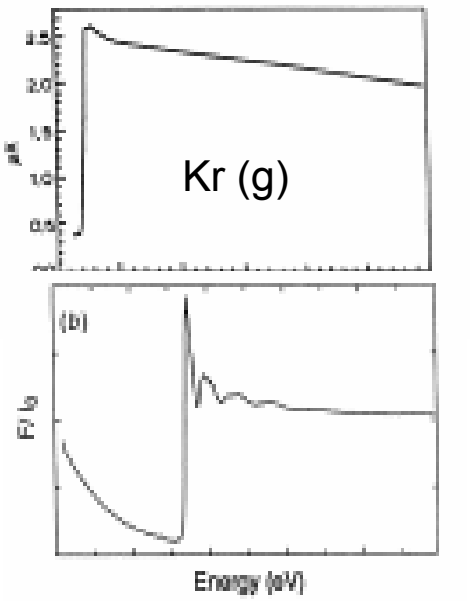


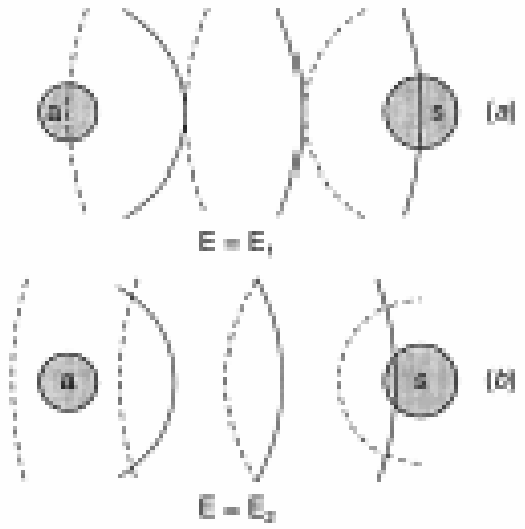


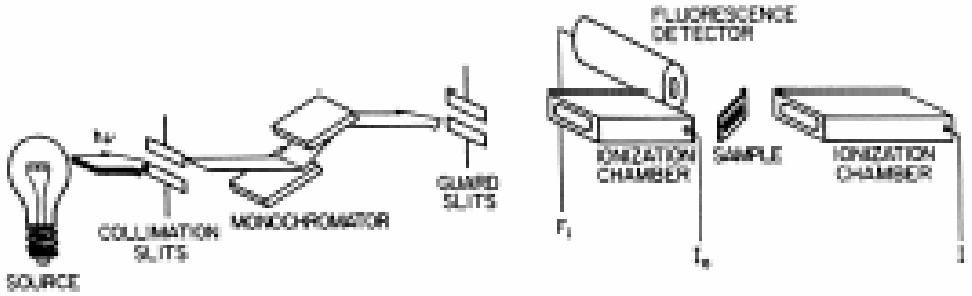
LOCAL PROBES:

3) EXAFS (basics)

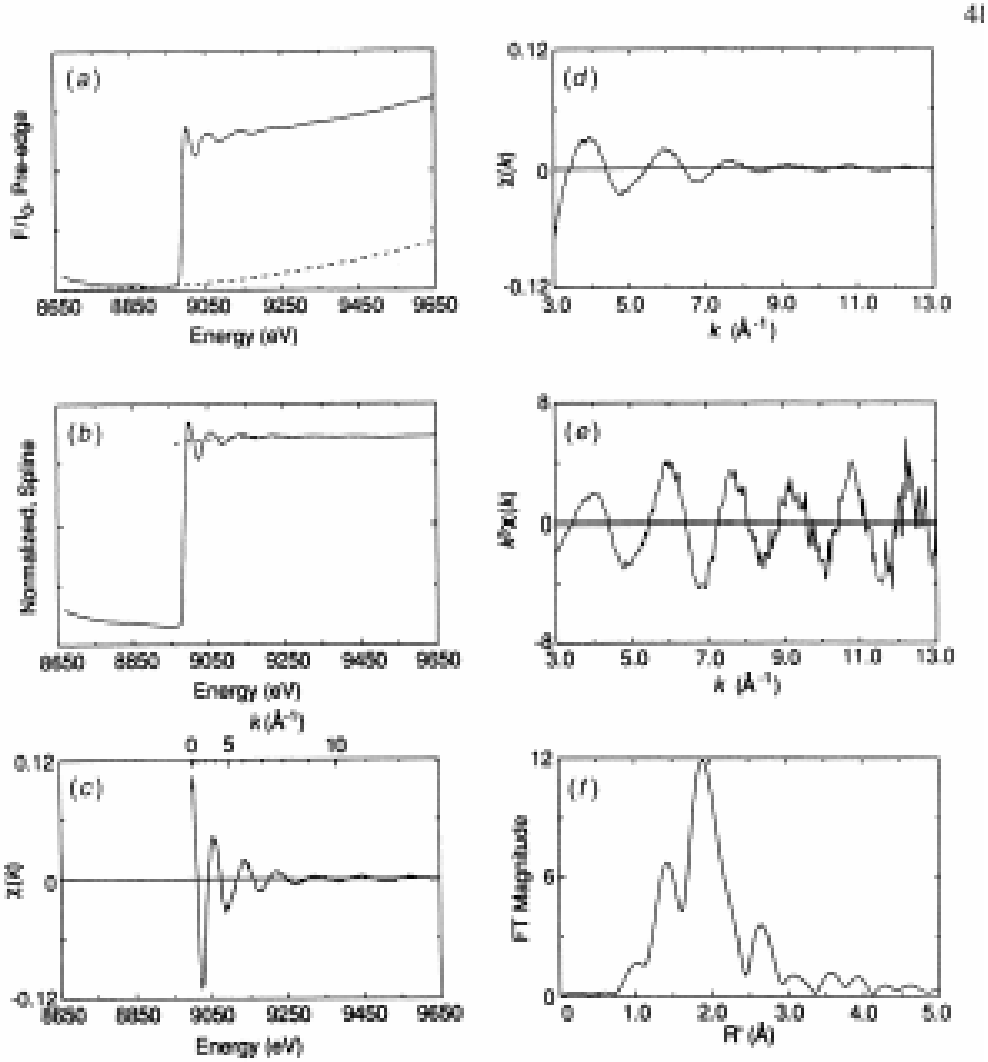




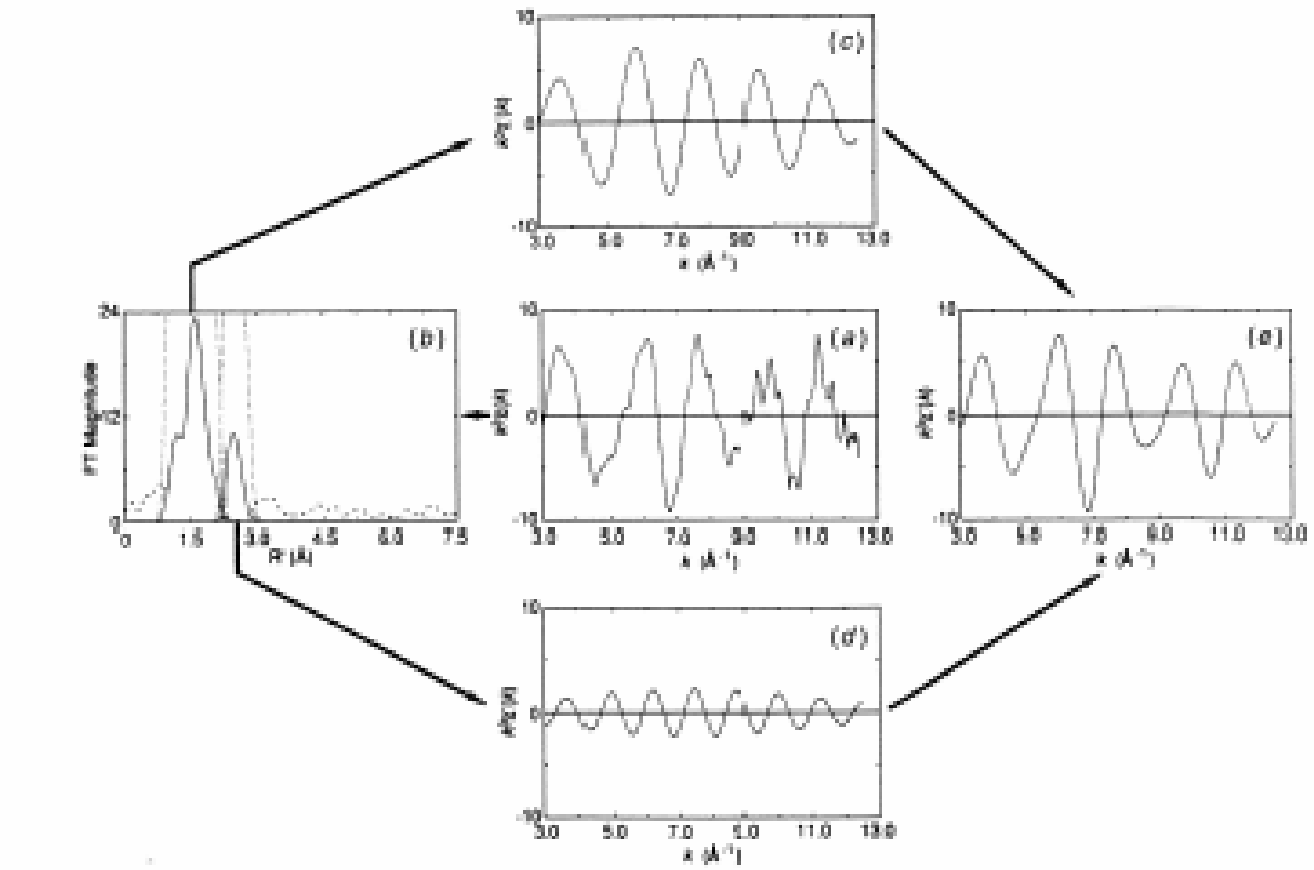




LOCAL PROBES: 3) EXAFS (basics: signal extraction)



LOCAL PROBES: 3) EXAFS (basics: signal analysis)

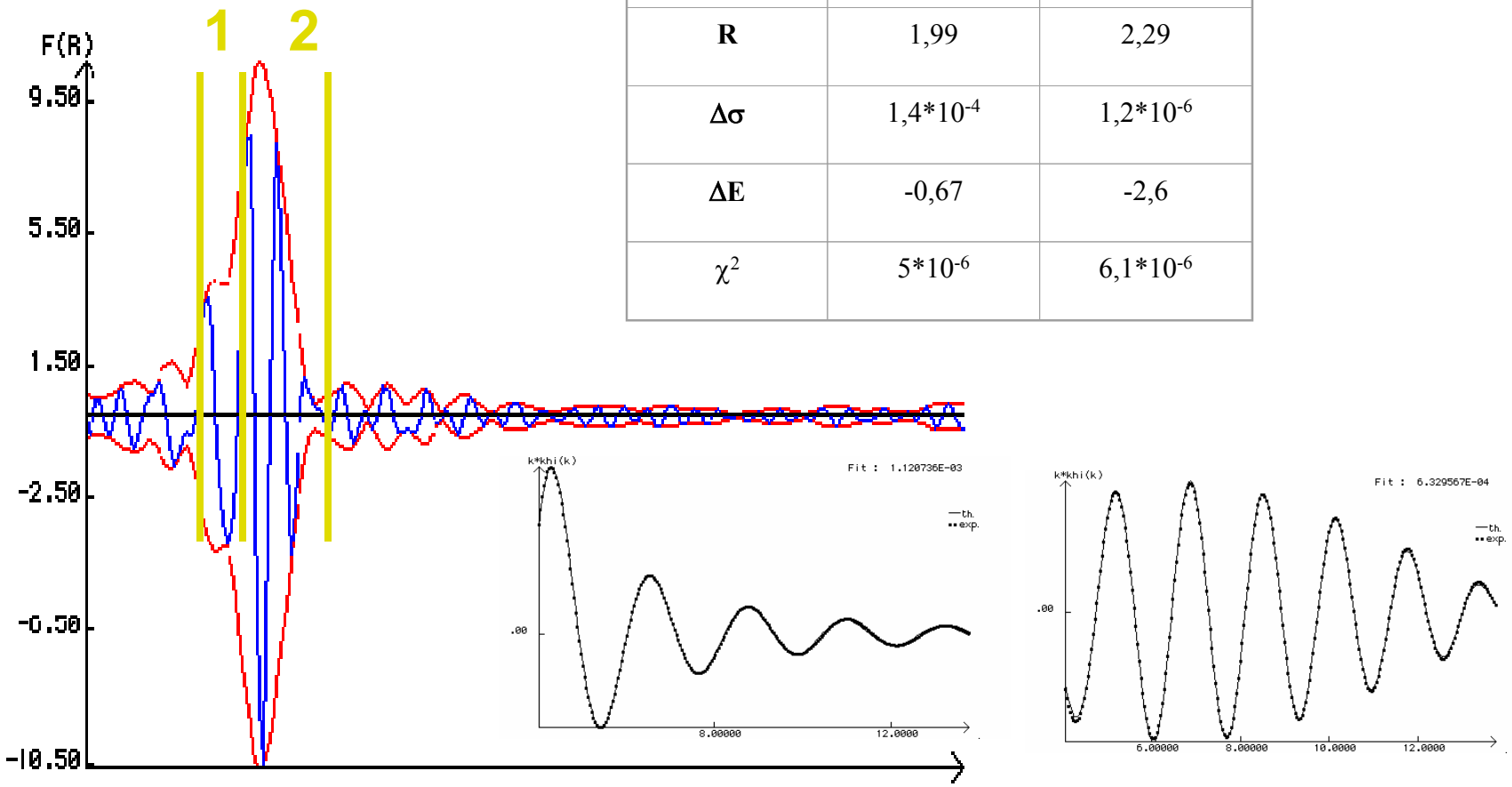


$$\chi(k) = \sum N_s \left(f_s(\pi,k)/k\, R_{as}^2 \right) \exp(-R_{as}/\lambda_f) \exp(-2\sigma_{as}^2 k^2) \sin(2kR_{as} + \alpha_{as}(k))$$

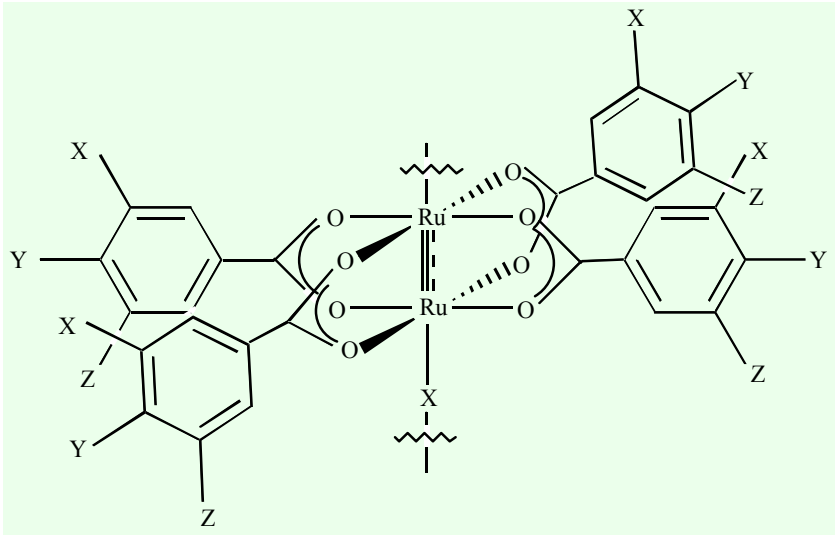
LOCAL PROBES:

3) EXAFS (Results)

	1 Shell	2 Shell
Element	O	Ru
N	4,04	0,84
R	1,99	2,29
Δσ	$1,4*10^{-4}$	$1,2*10^{-6}$
ΔE	-0,67	-2,6
χ^2	$5*10^{-6}$	$6,1*10^{-6}$



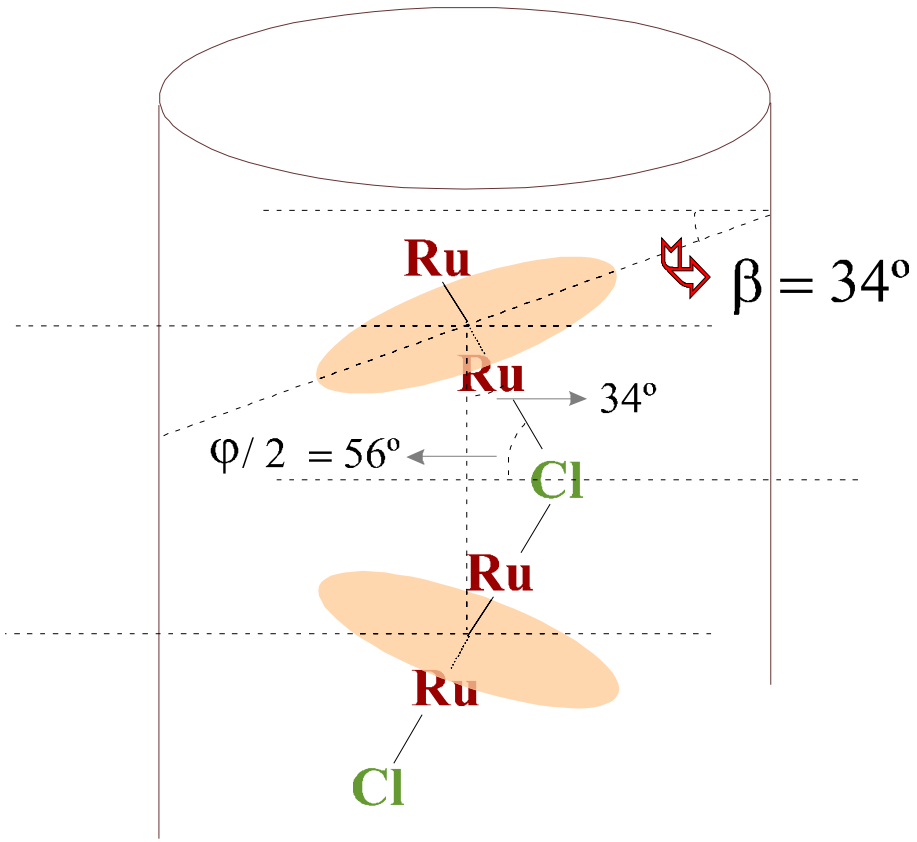
Stereoch. Asp. Metallomesogens – Ex. #3 (Model for $Ru_2(B3OCn)_4Cl$)

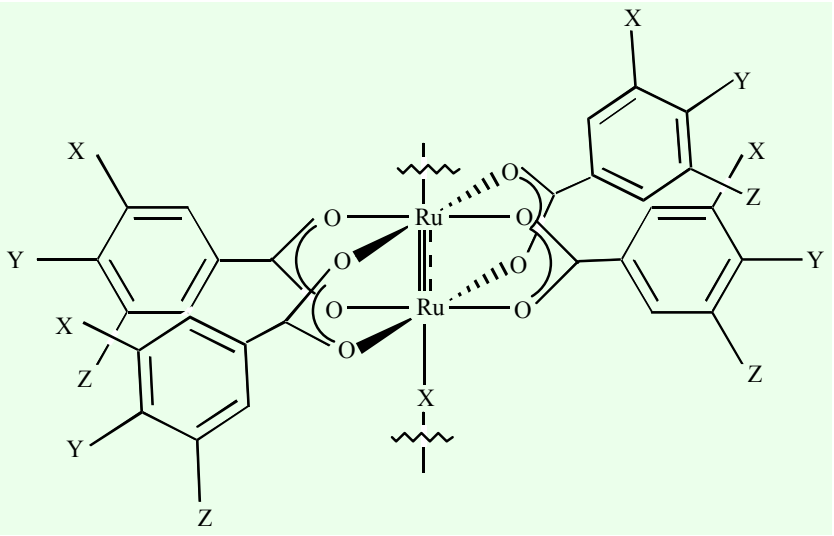


Binuclear "Molecular" structure
retained in the mesophase

Stereoch. Asp. Metallomesogens – Ex. #3 (Model for $Ru_2(B3OCn)_4Cl$)

Proposed Model (2001)





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Chaia *et al*, *Mol. Cryst. Liq. Cryst*. **330**, 213 (1999)
Rusjan *et al*, *Langmuir* **18**, 10116 (2002)

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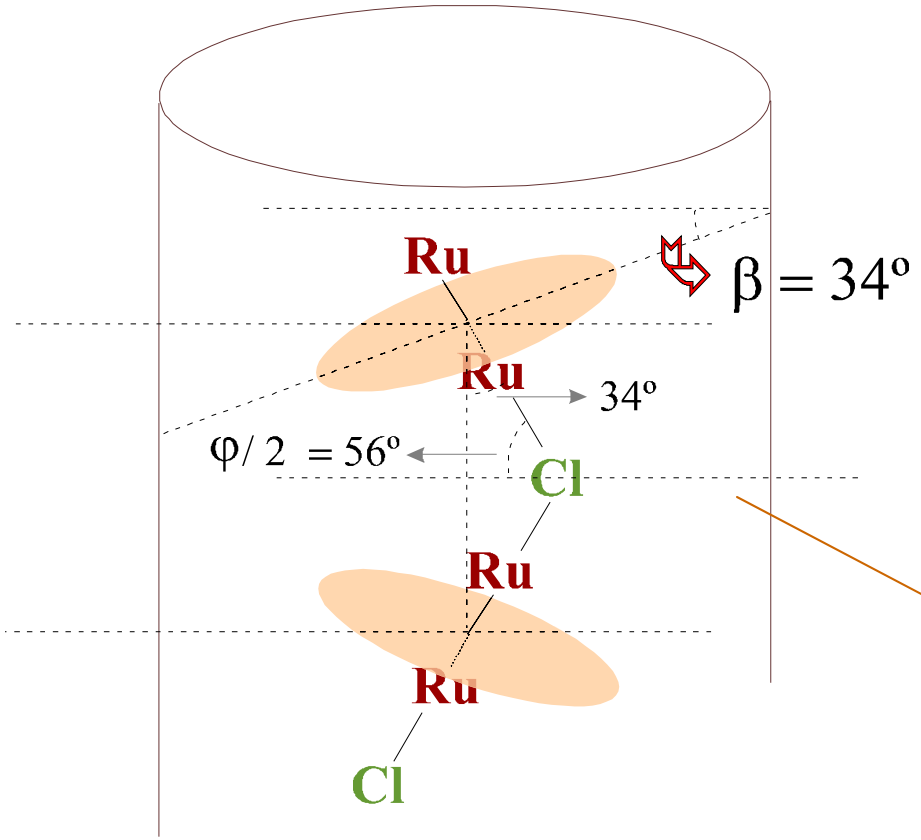

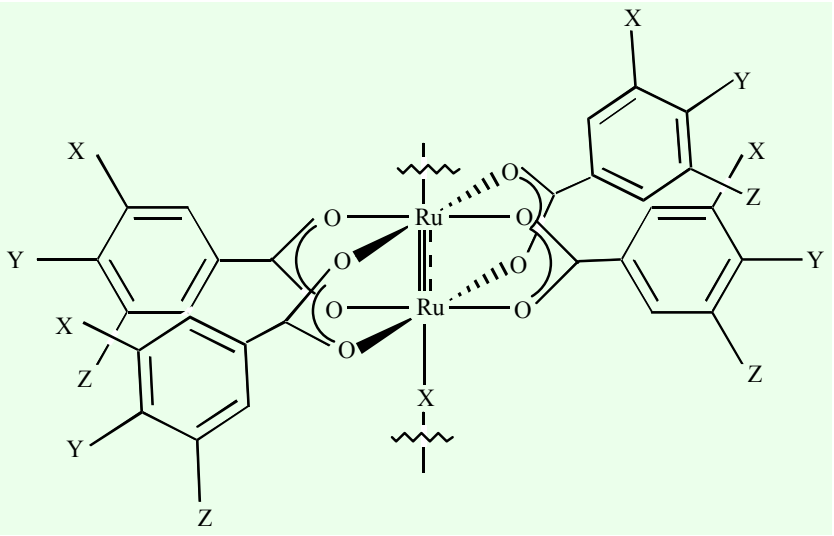

Binuclear "Molecular" structure
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* **Orbital overlap**
* **Packing efficency**
* **Microsegregation**

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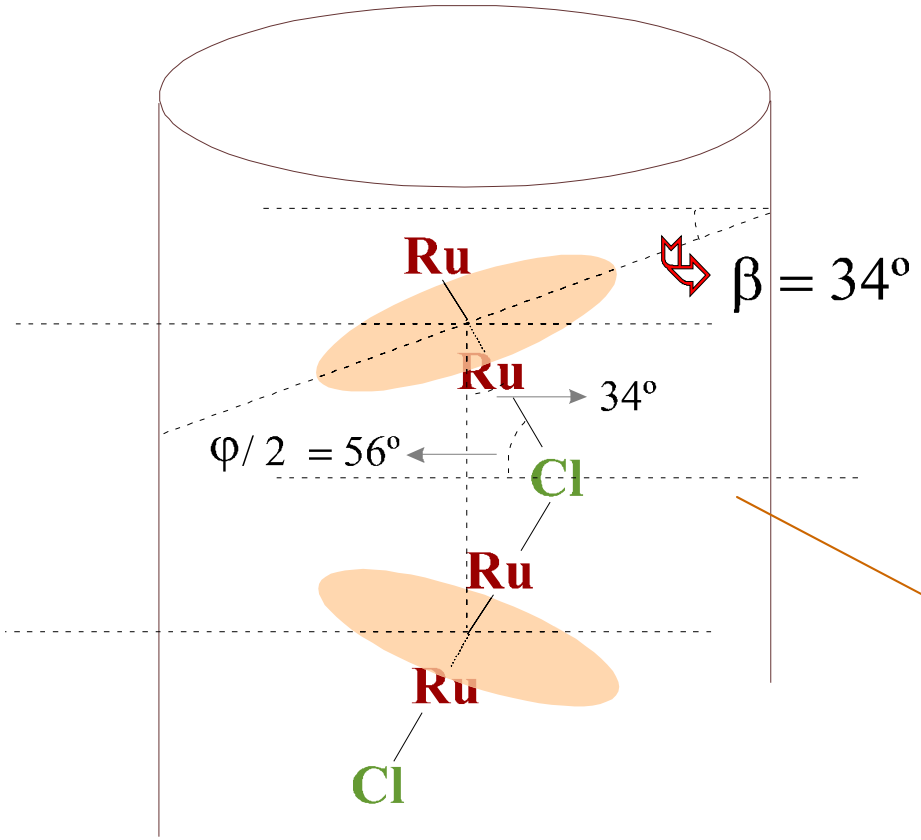

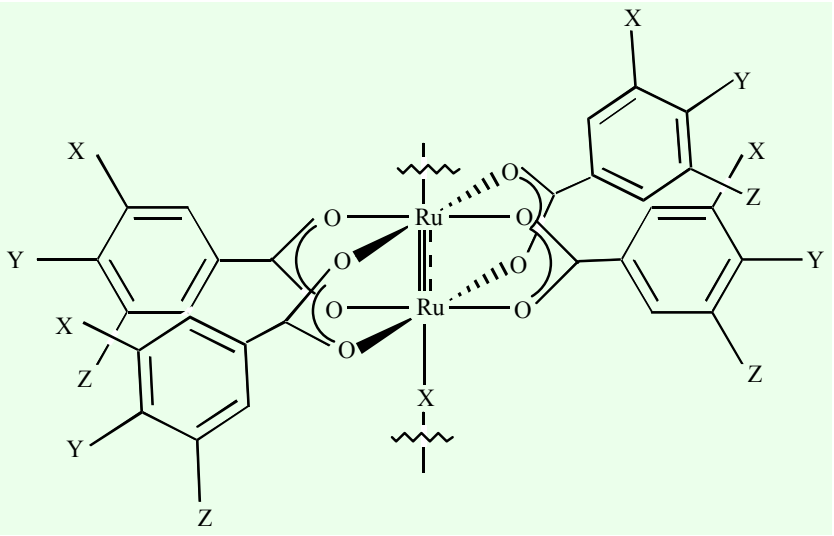

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Role of coordination bonds

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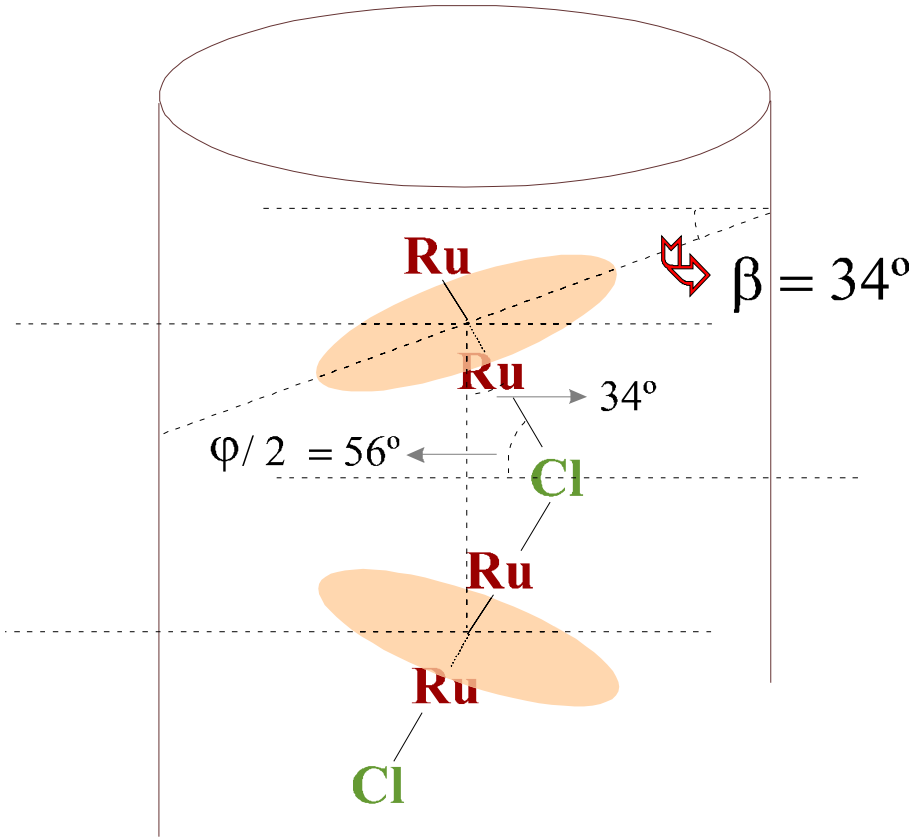

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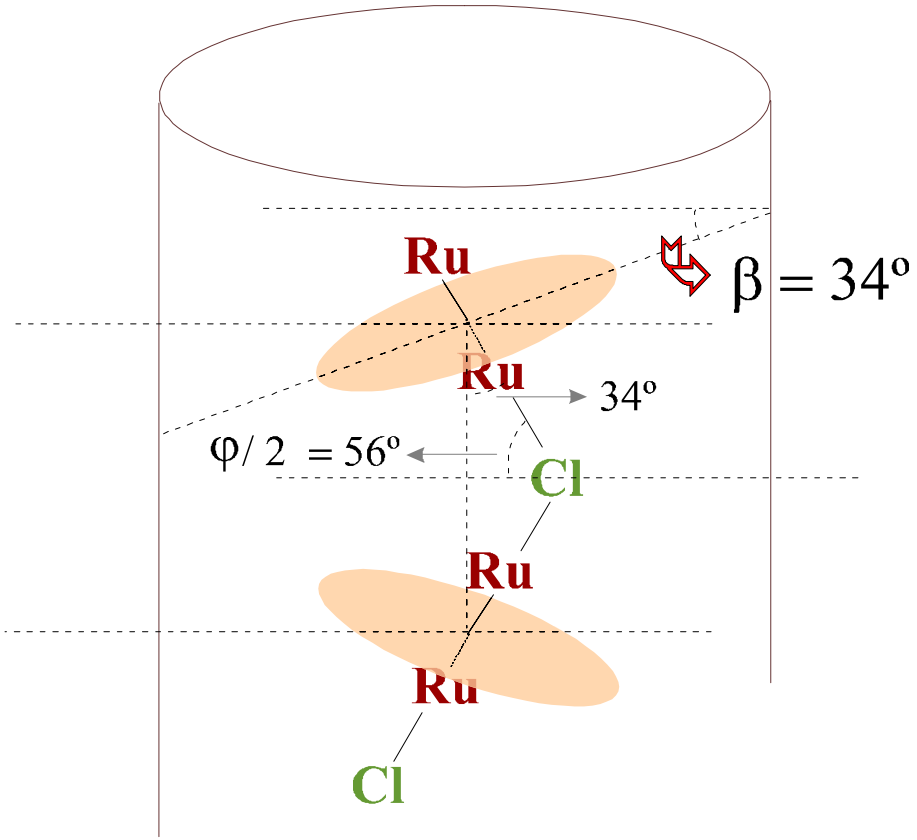
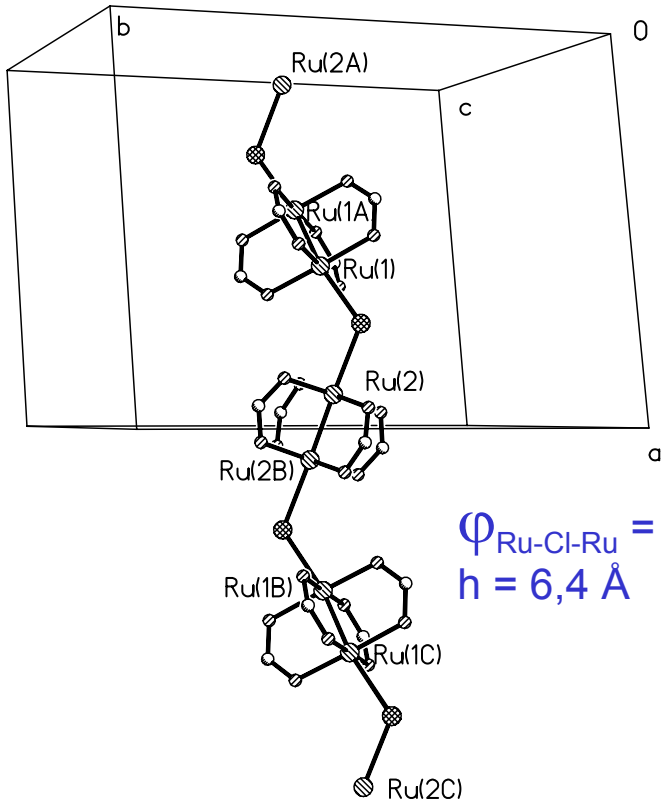


Chaia *et al*, *Mol. Cryst. Liq. Cryst*. **330**, 213 (1999)
Rusjan *et al*, *Langmuir* **18**, 10116 (2002)

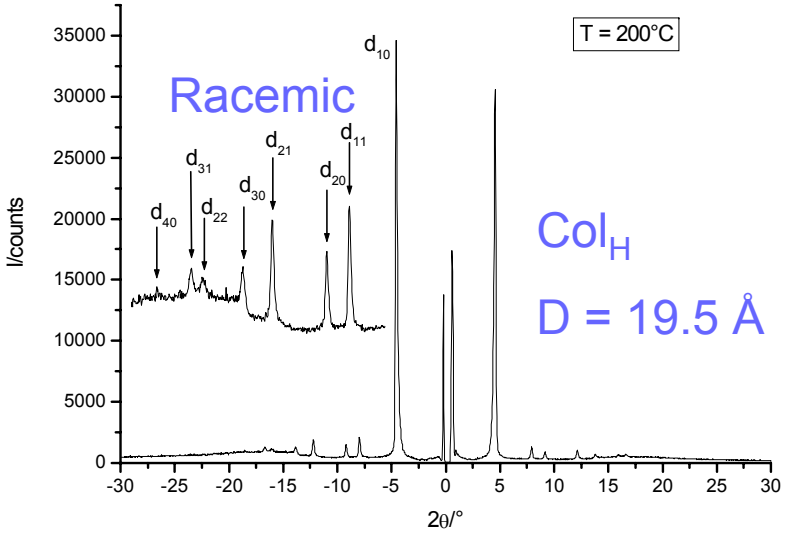
Crystalline structure of a short chain homolog (2004)

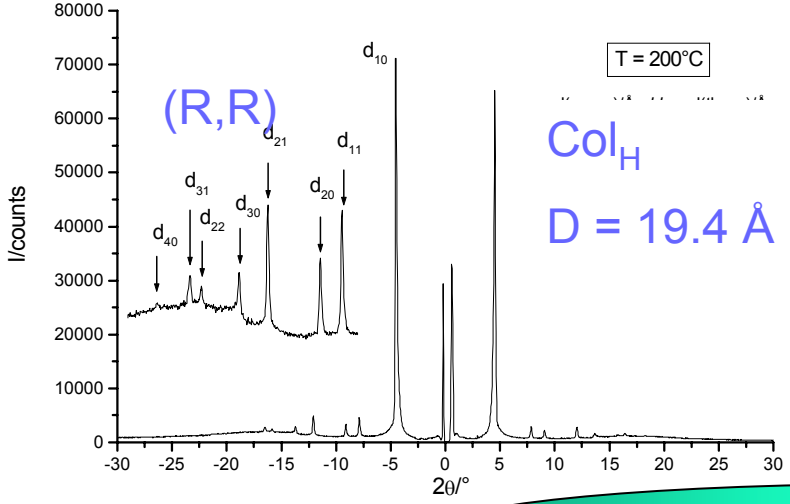


$\varphi_{Ru\text{-}Cl\text{-}Ru}$ = 116º
h = 6,4 Å

Persello, Gómez, Fagnola, Baggio, *et al* (to be sent)

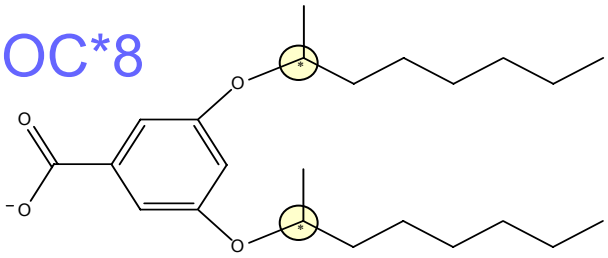
VII – Chiral centers at $R_{eq}CO_2$: Preliminary results

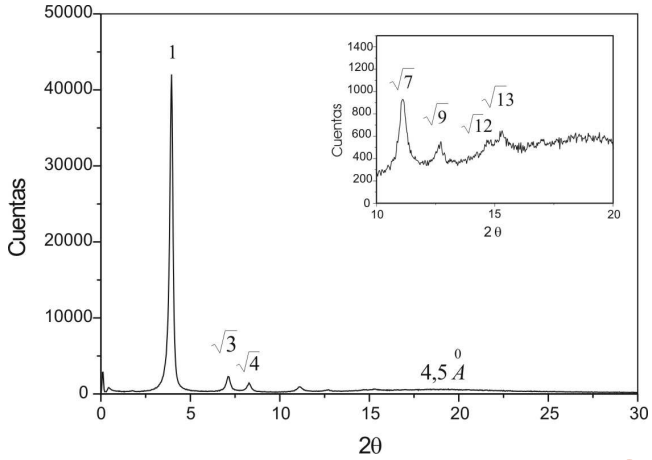




Chiral equatorial ligand:

3,5-B2OC*8





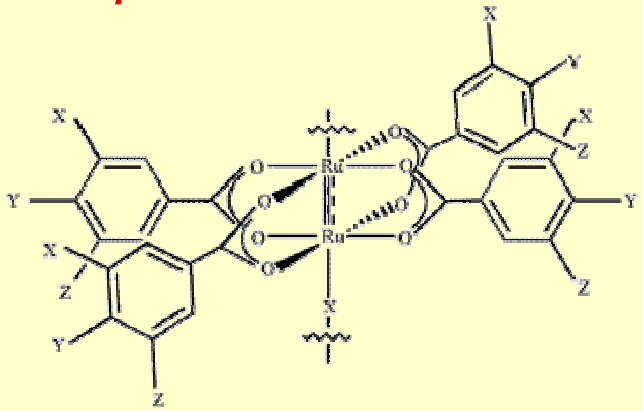
Linear equatorial ligand: 3,5-B2OC10

Col_H at RT; D = 20.4 Å

Role of coordination bonds

4th example: Lyotropic polymeric dirhutenium carboxylates

Supramolecular changes by solvent addition



Aims:

- Decrease melting temperatures

- Decrease viscosity

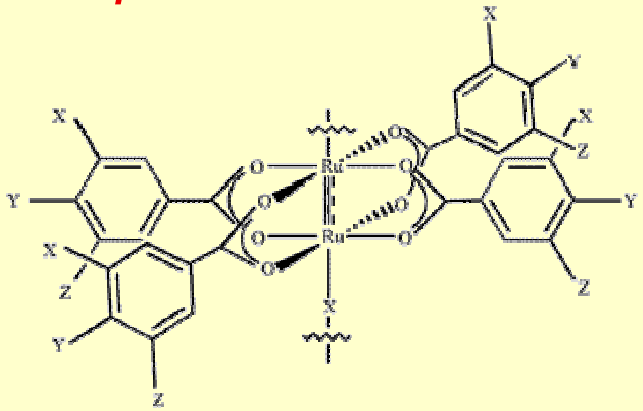
Compound	X	Y	Z
$Ru_2(3,4,5\text{-}B3OC14)_4Cl$	$OC_{14}H_{29}$	$OC_{14}H_{29}$	$OC_{14}H_{29}$
$Ru_2(3,4\text{-}B2OC14)_4Cl$	$OC_{14}H_{29}$	$OC_{14}H_{29}$	H
$Ru_2(3,5\text{-}B2OC14)_4Cl$	$OC_{14}H_{29}$	H	$OC_{14}H_{29}$

$+ C_{12}H_{26}$

Rusjan *et al*, *Langmuir.* **18**, 10116 (2002)

4th example: Lyotropic polymeric dirhutenium carboxylates

Supramolecular changes by solvent addition



Compound	X	Y	Z
Ru_2(*3,4,5*-B3OC14)$_4$Cl	$OC_{14}H_{29}$	$OC_{14}H_{29}$	$OC_{14}H_{29}$
Ru_2(*3,4*-B2OC14)$_4$Cl	$OC_{14}H_{29}$	$OC_{14}H_{29}$	H
Ru_2(*3,5*-B2OC14)$_4$Cl	$OC_{14}H_{29}$	H	$OC_{14}H_{29}$

$+ C_{12}H_{26}$

Aims:

- Decrease melting temperatures

- Decrease viscosity

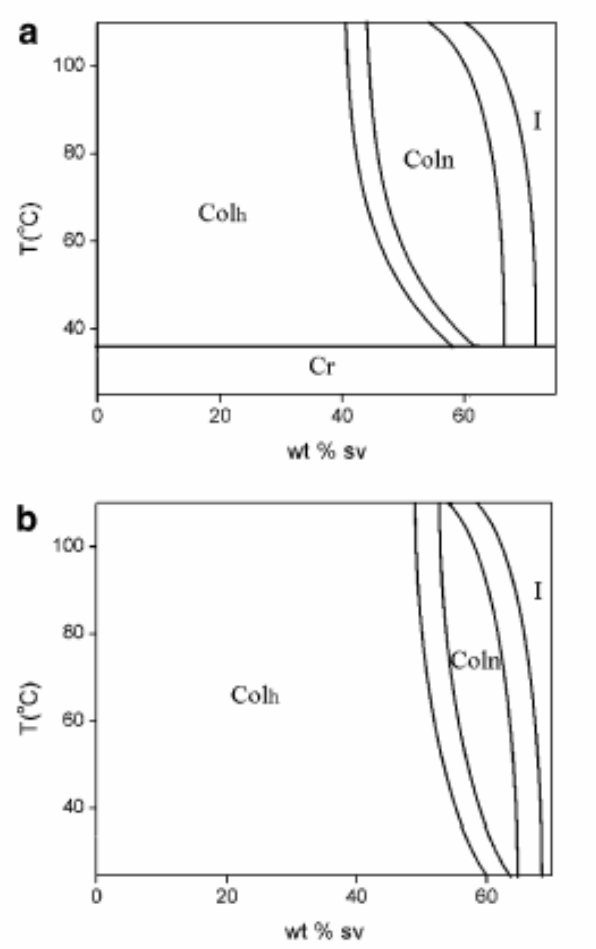
1st observation:

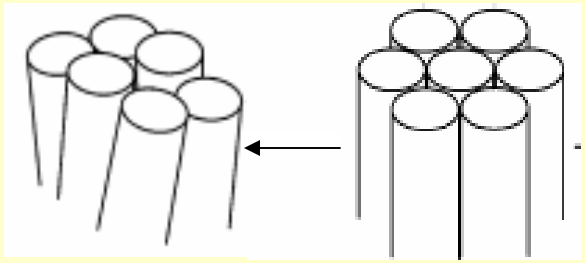
Progressive decrease of melting temperatures with added solvent

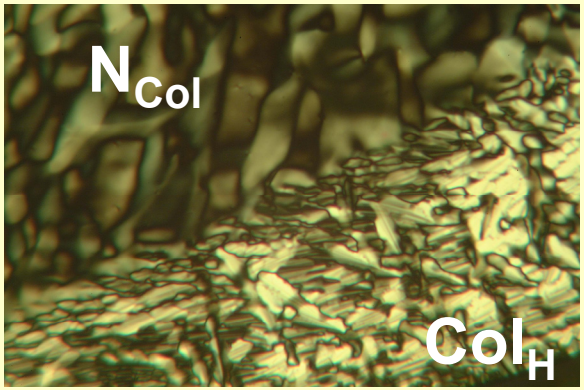
Rusjan *et al*, *Langmuir.* **18**, 10116 (2002)

Stereochemical Aspects of Metallomesogens – Example # 4

2nd observation: Phase diagrams and sequences







Stereochemical Aspects of Metallomesogens – Example # 4

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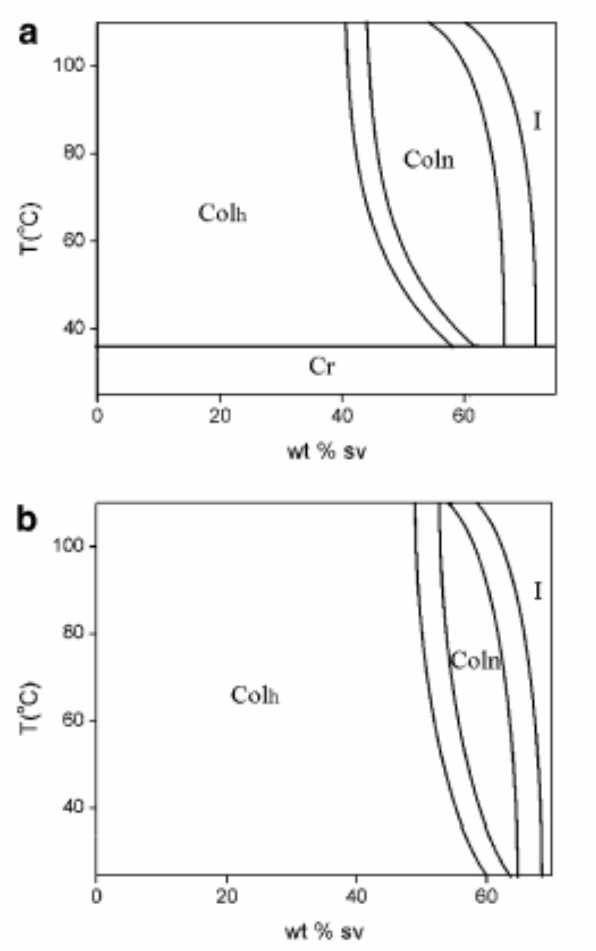
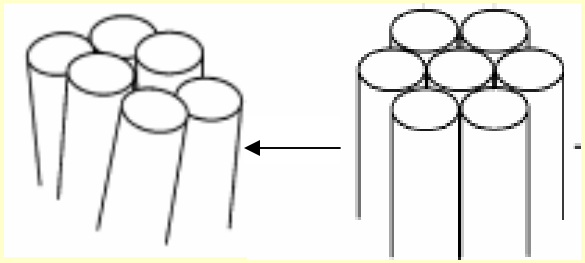
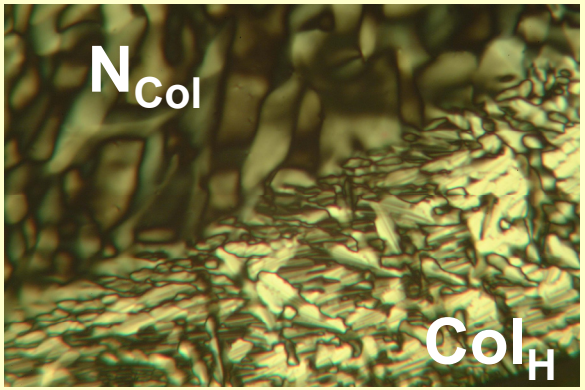
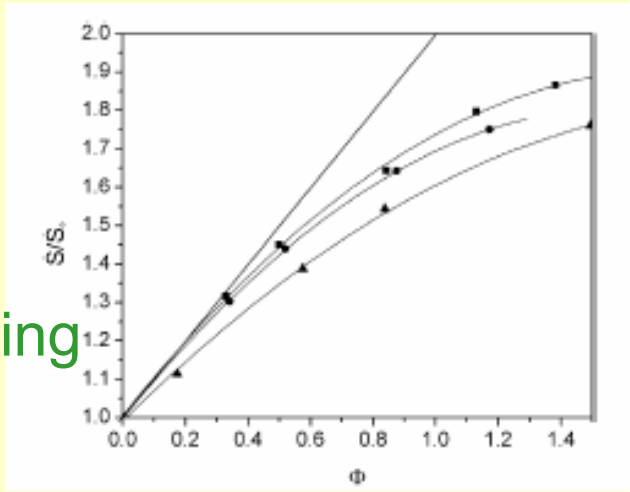


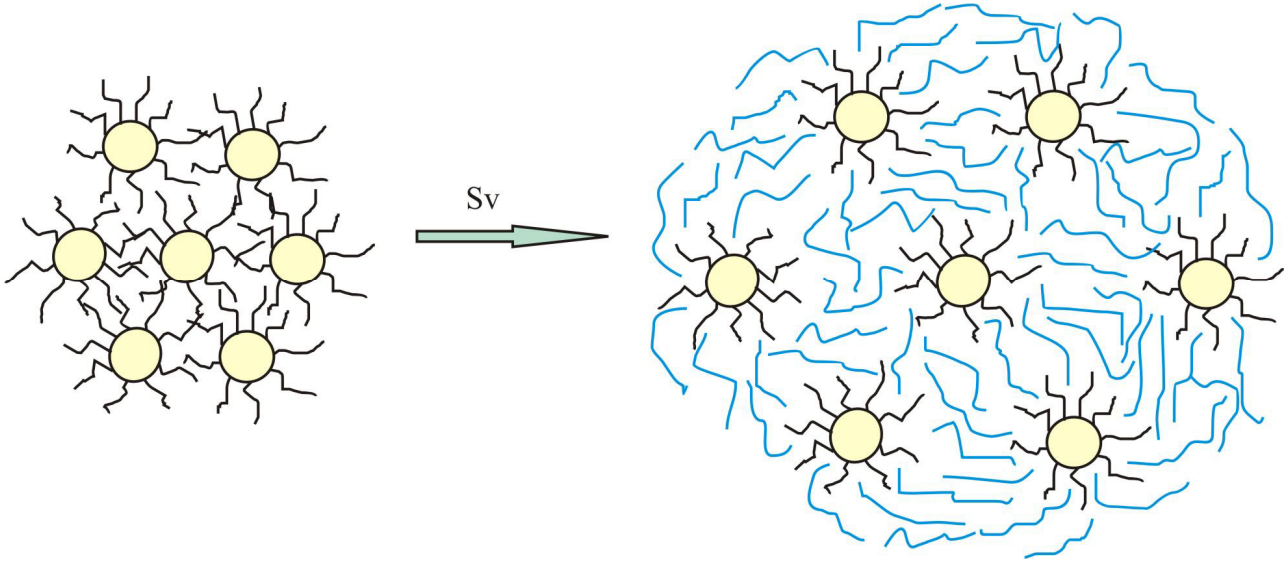




3rd observation: Swelling of the Col_H phase



Stereochemical Aspects of Metallomesogens – Example # 4



4th observation: Structural analysis of the swelling process

Φ = volumetric fraction of added sovent

$$\Phi = \frac{C\,\bar{v}_d}{(1\text{-}C)\,\bar{v}_c}$$

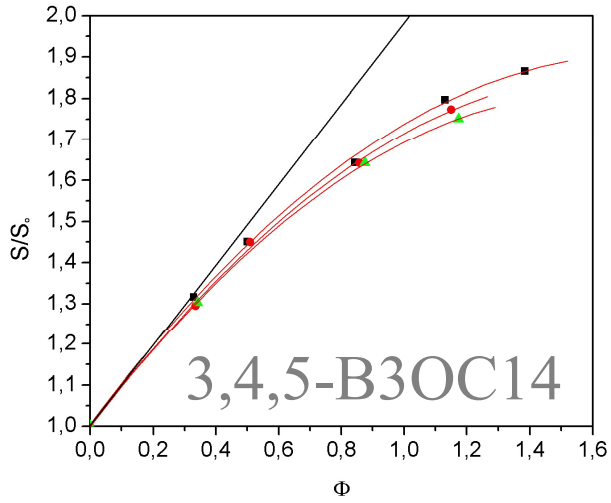
Assuming additive volumes:

$$V=V_o+V_o\Phi \quad \Rightarrow \quad Sh=S_oh_o+S_oh_o\Phi$$

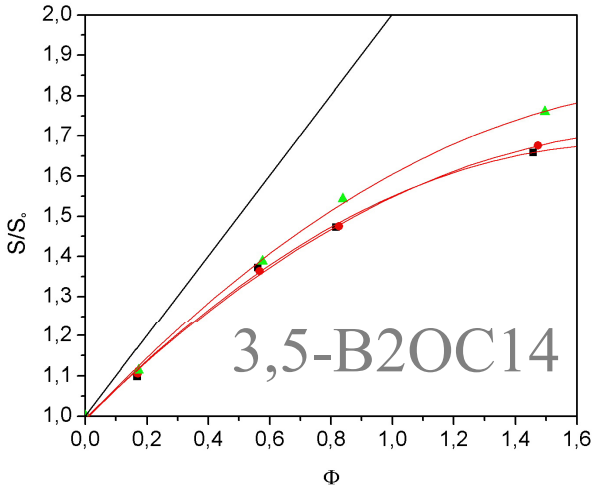
and $h = h_o \Rightarrow S/S_o=1+\Phi$ linear (slope = 1)

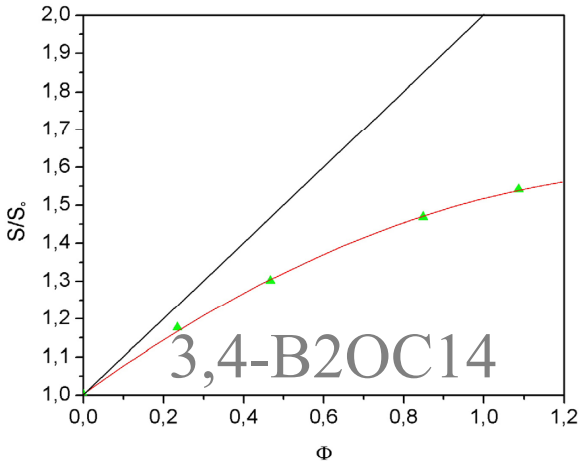
Stereochemical Aspects of Metallomesogens – Example # 4

Structural analysis of the swelling process



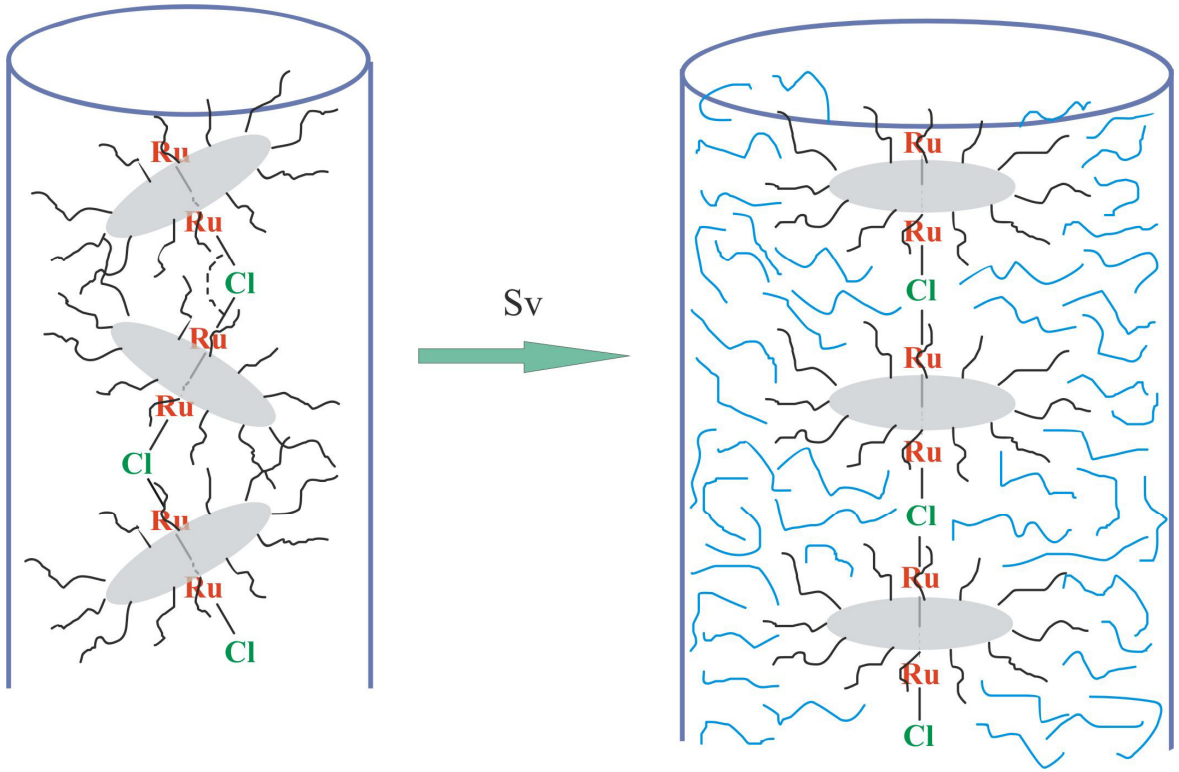
40°C
70°C
100°C





Stereochemical Aspects of Metallomesogens – Example # 4

Structural analysis of the swelling process - a possibe explanation: change in poymeric chains conformation



+ Orbital overlap

+ Packing efficency

+ Microsegregation

Added solvent might relax last 2 constraints, allowing the orbital overlap taking its best value

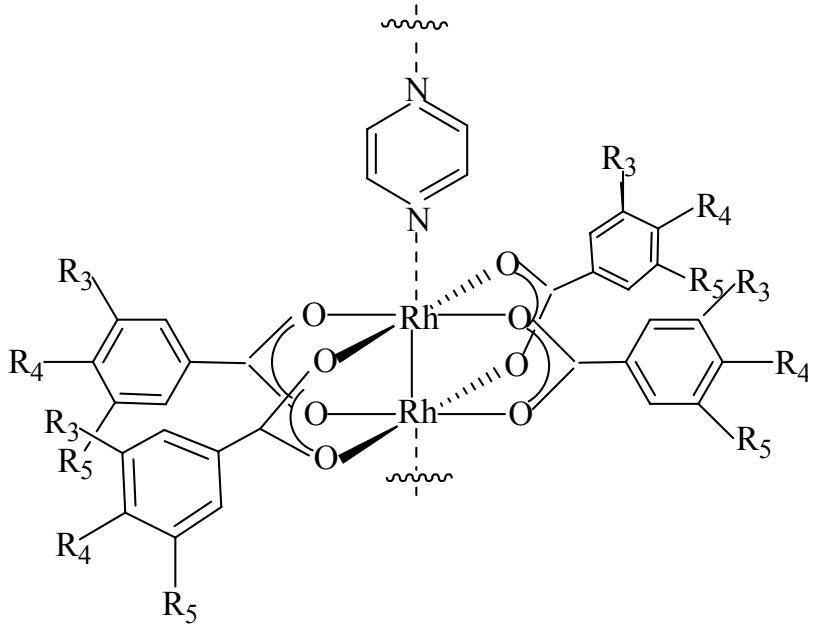
5th example: Columnar mesophases in rhodium "neutral" coordination polymers

Molecular shape and volume based design of thermotropic columnar "neutral" coordination polymers

Previous attempts to obtain columnar $M_2(O_2CR)_4BL$- polymers (Attard, Serrano, Van Hecke, Cukiernik, Chisholm): unsuccesful

Strategy (again!):

Intracolumnar filling of the intermolecular space by using bulky equatorial carboxylates



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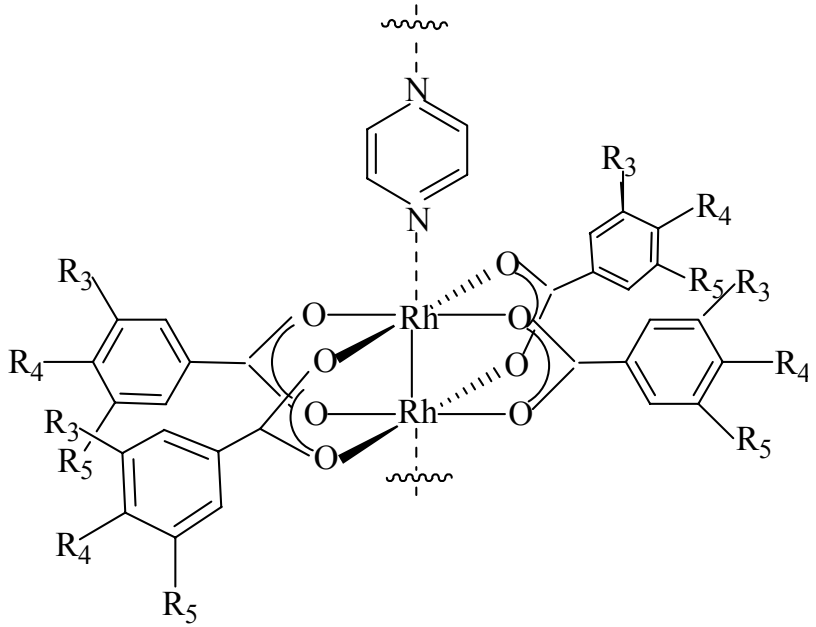

- Job UV/Vis
- elem. an.
- FTIR
- NMR

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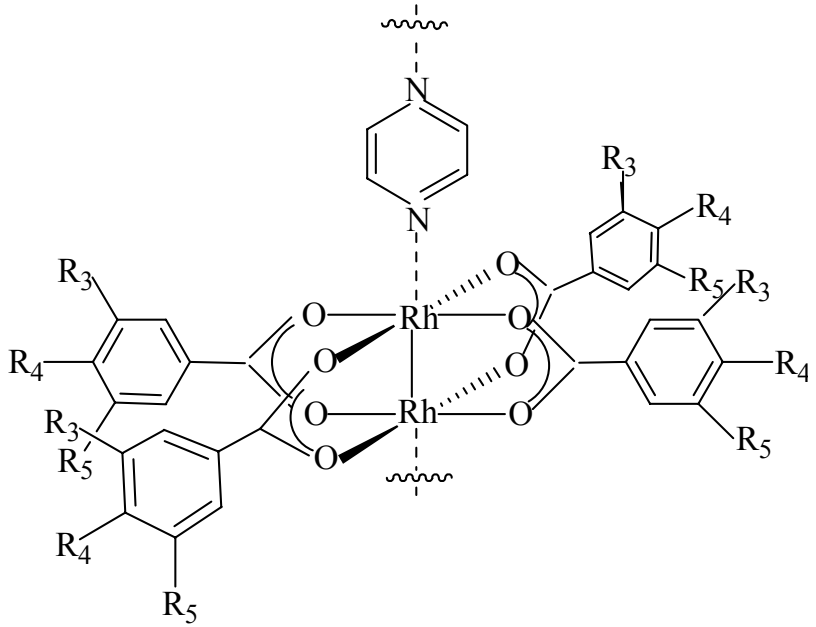

- Job UV/Vis
- elem. an.
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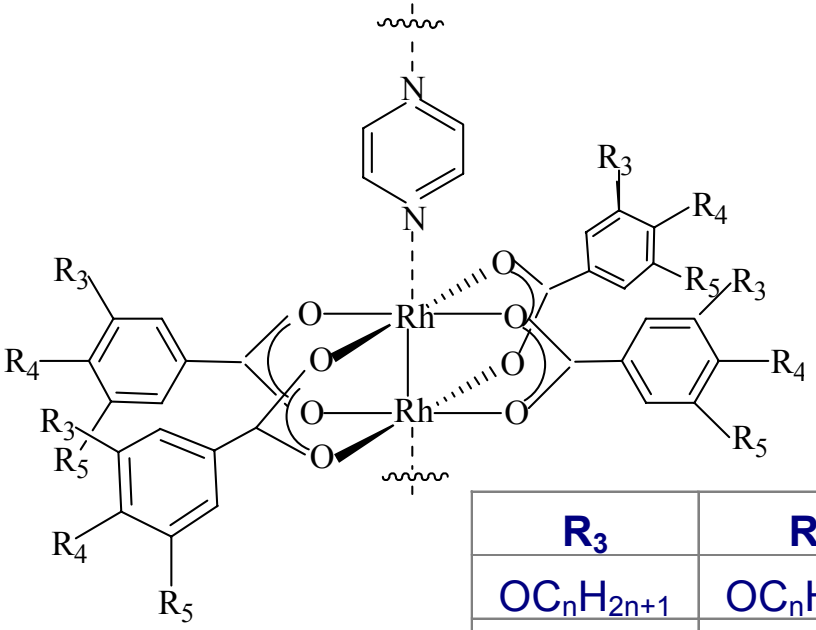
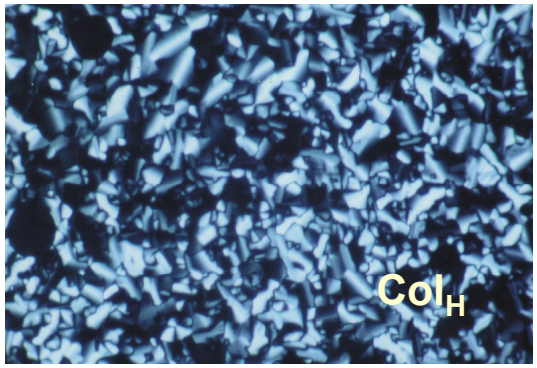
I – Mesomorphic behaviour



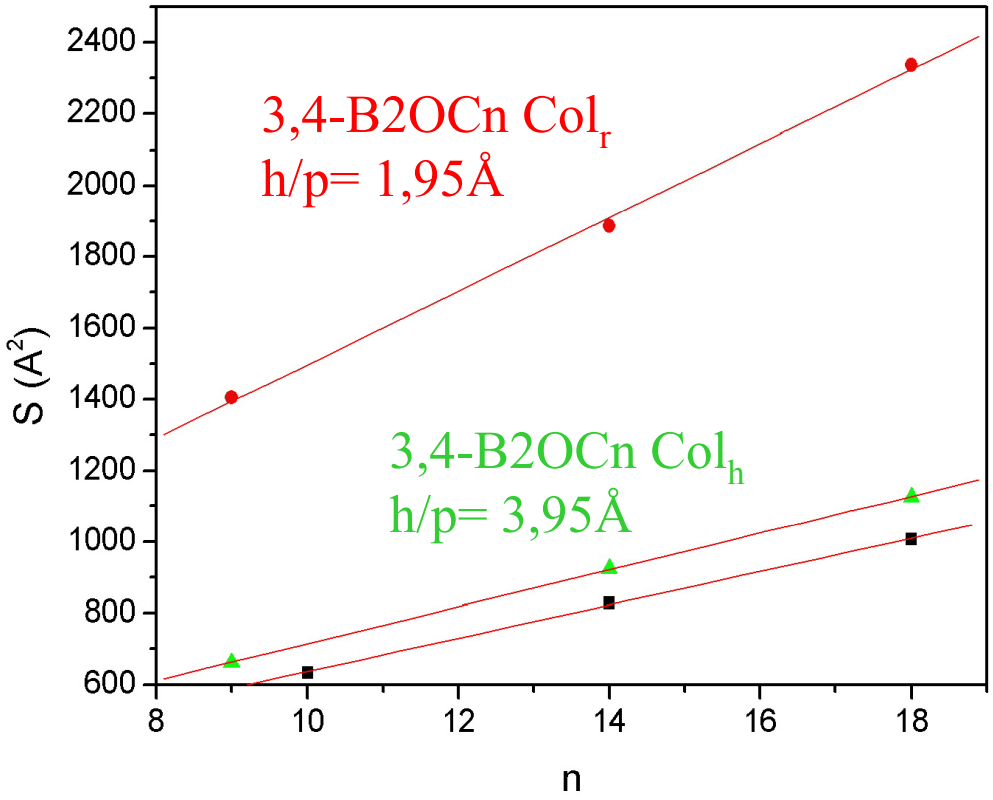


R_3	R_4	R_5	pz	LC properties
OC_nH_{2n+1}	OC_nH_{2n+1}	H	--	Col_H // Col_R
OC_nH_{2n+1}	H	OC_nH_{2n+1}	--	Col_H
OC_nH_{2n+1}	OC_nH_{2n+1}	OC_nH_{2n+1}	--	Col_H
OC_nH_{2n+1}	OC_nH_{2n+1}	H	YES	Col_R // Cub
OC_nH_{2n+1}	H	OC_nH_{2n+1}	YES	N_{Col}
OC_nH_{2n+1}	OC_nH_{2n+1}	OC_nH_{2n+1}	YES	Col_H

Rusjan *et al*, *Chem. Mater.* **14**, 1564 (2002)

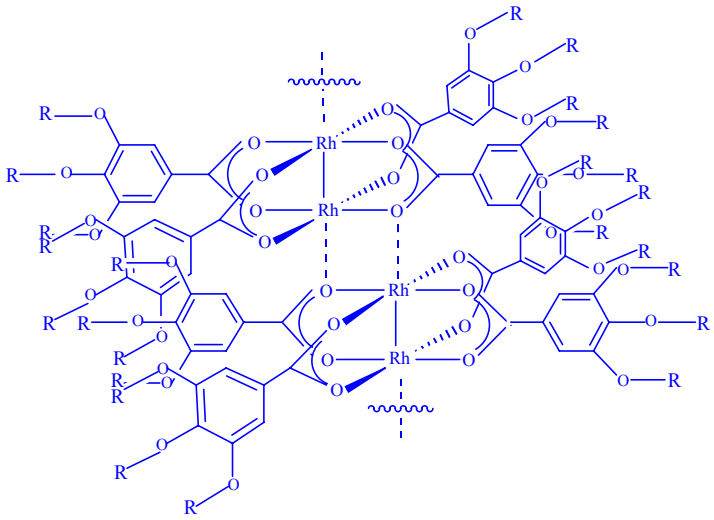
II – Supramolecular models for the precursors

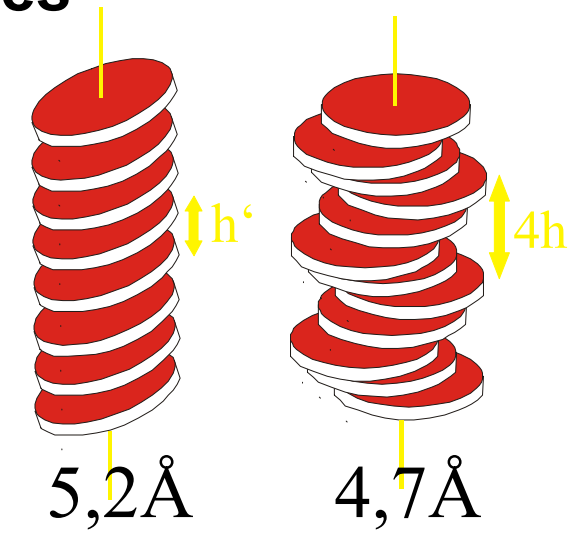
$$S=(p/h).[V_{pc} + 4m.\Delta V\ CH_3] + (p/h).[4m.VCH_2].n$$



3,4,5-B3OCn Col_h
h/p= 7,2Å

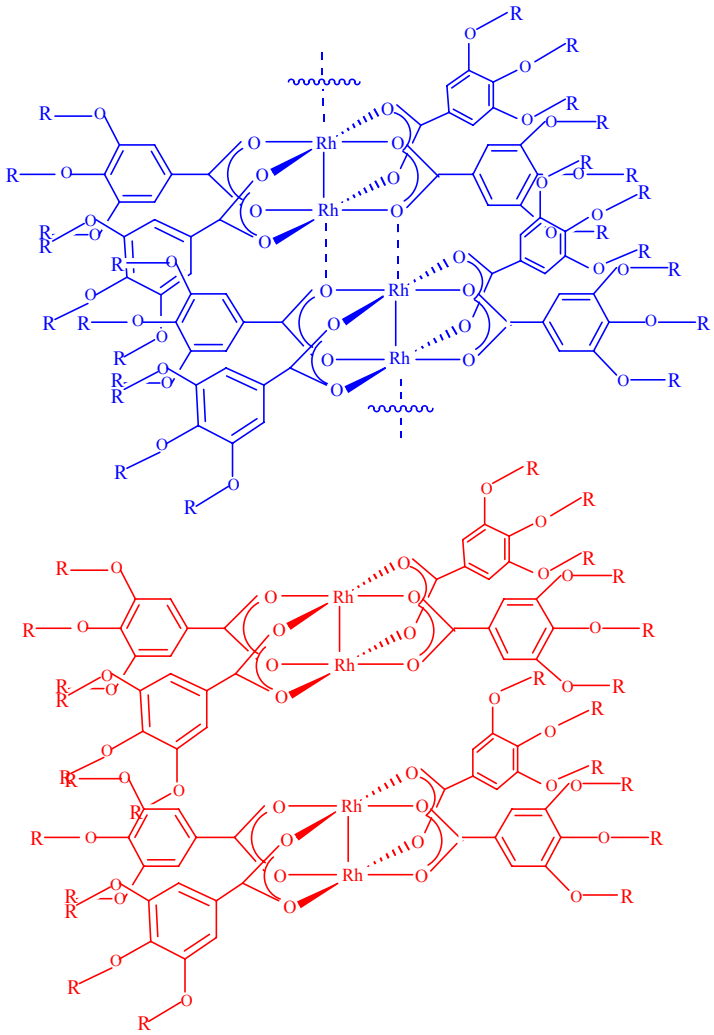
$Rh_2(3,4,5\text{-}B3OCn)_4$ Series

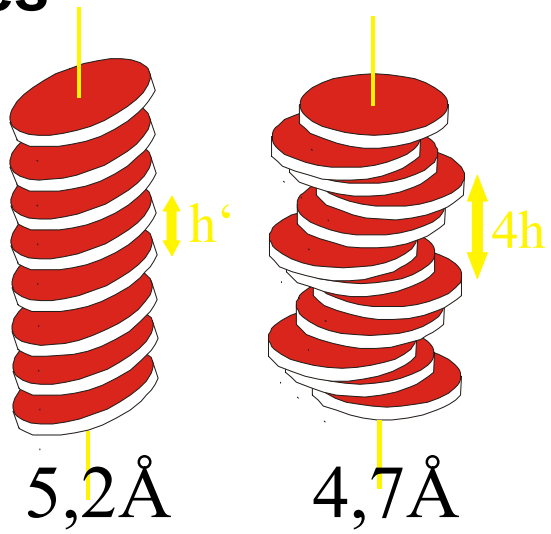




h/p = 7,2(4)Å

$Rh_2(3,4,5\text{-}B3OCn)_4$ Series





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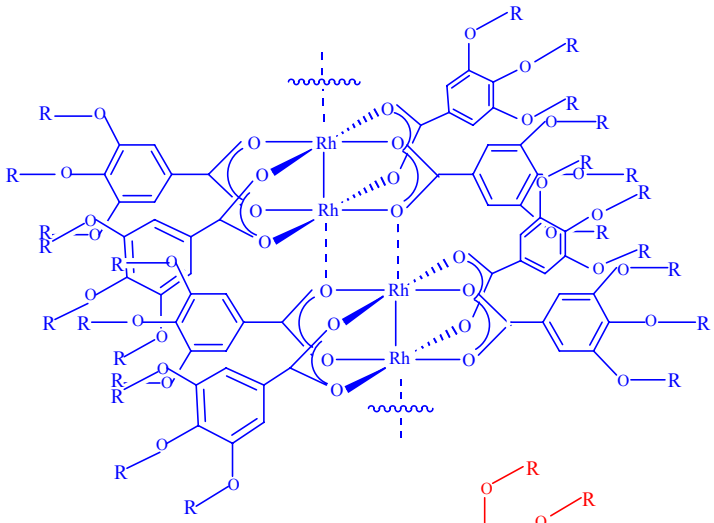

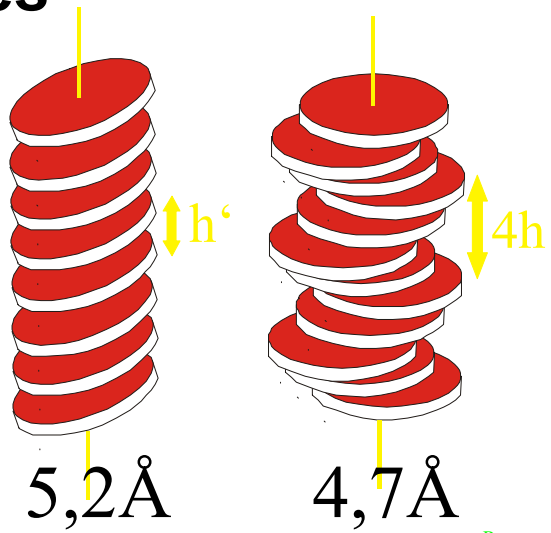

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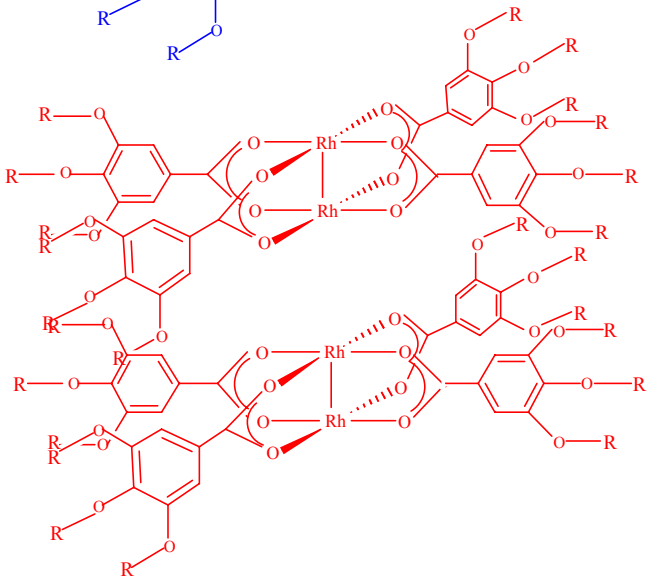
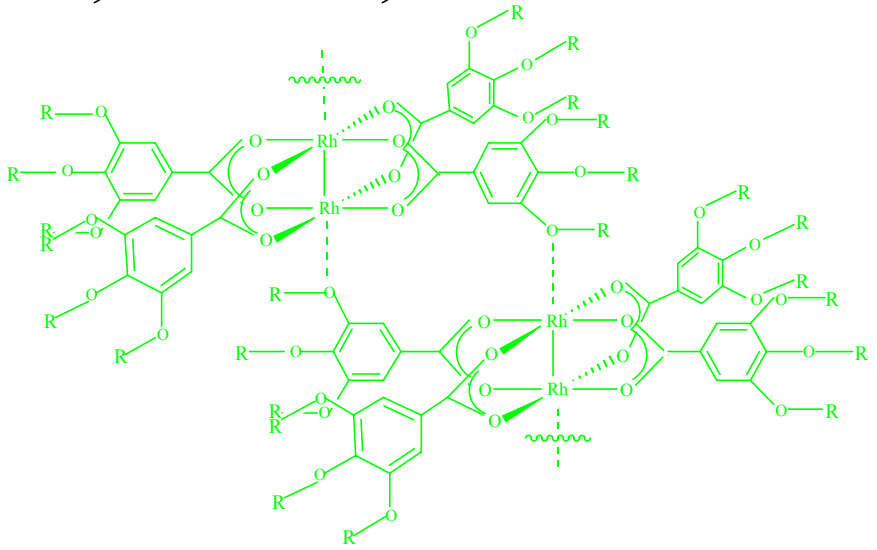
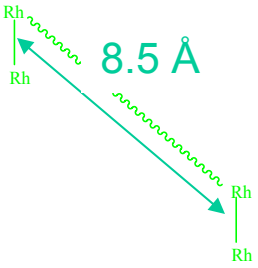
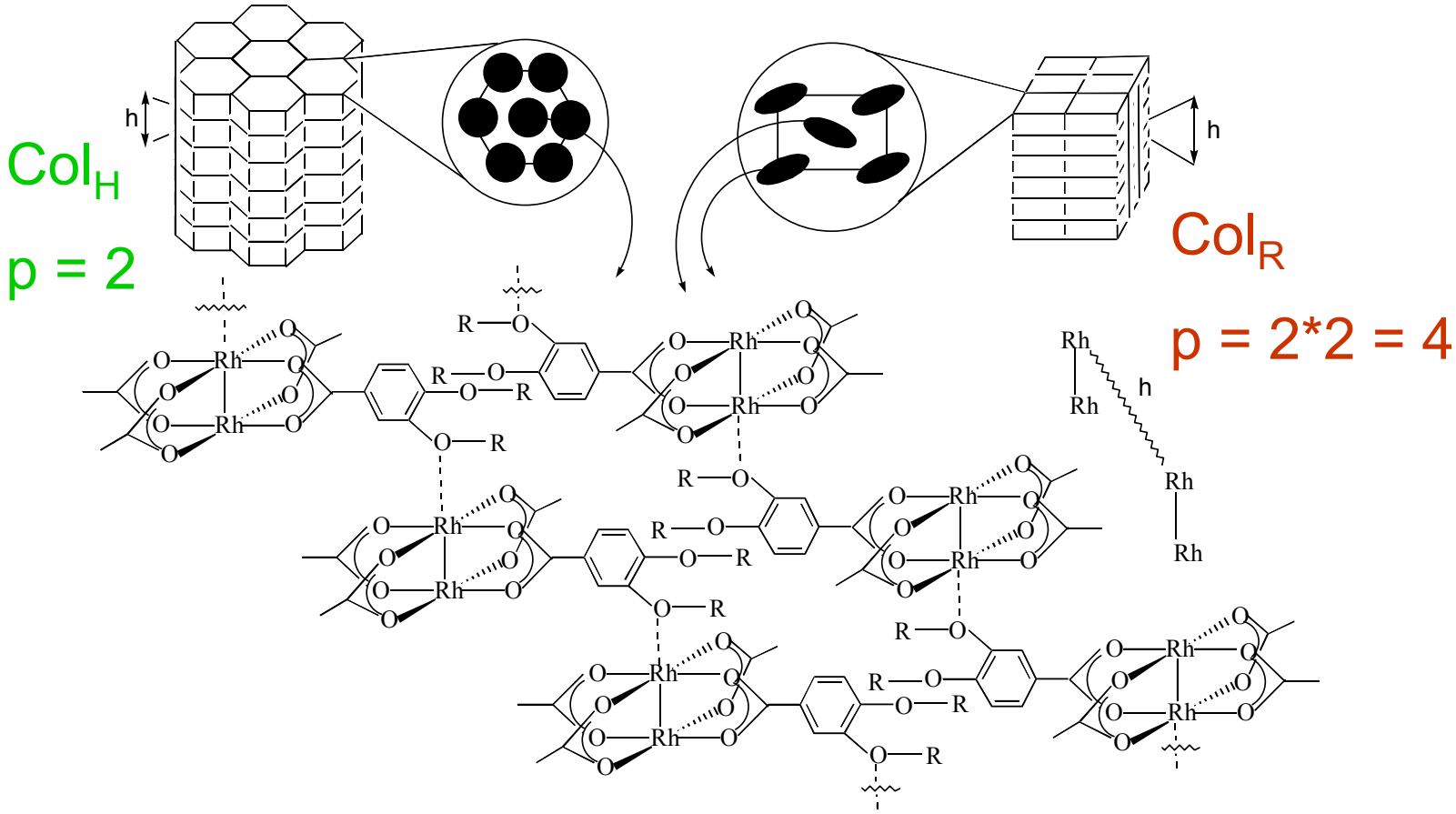






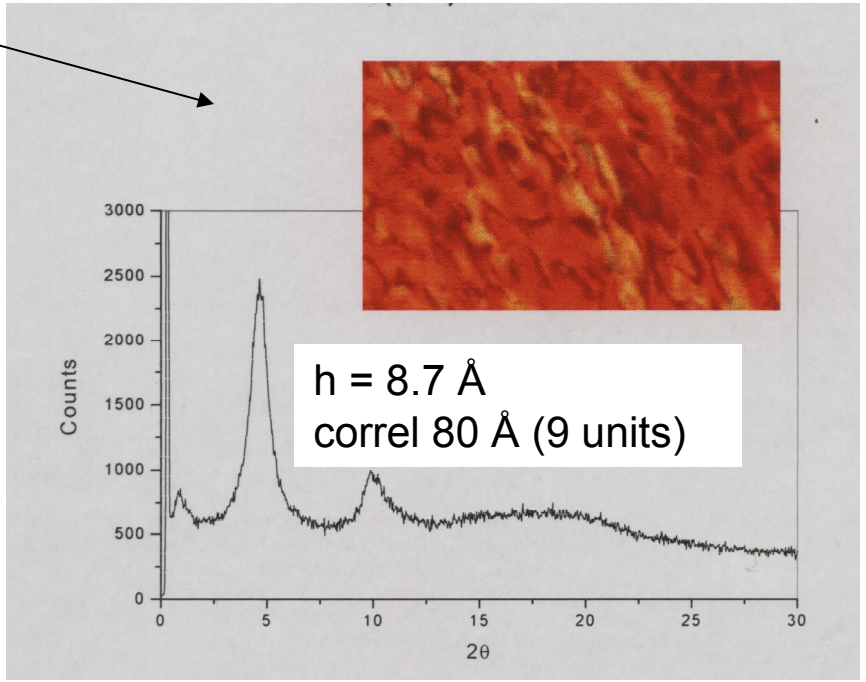
$Rh_2(3,4\text{-}B3OCn)_4$ Series



III – LC behavior & Supramolecular models for the polymers

Series	LC behaviour
$Rh_2(3,4\text{-}B2OCn)_4pz$	**Col_R // Cub**
$Rh_2(3,5\text{-}B2OCn)_4pz$	**N_{Col}**
$Rh_2(3,4,5\text{-}B2OCn)_4pz$	**Col_H**

h = 7.6 Å
correl 130 Å (17 units)



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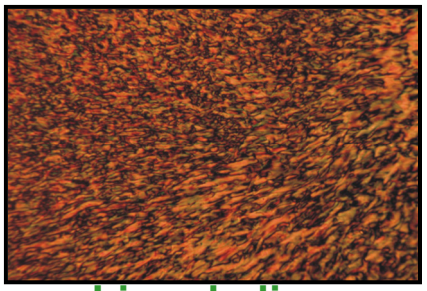
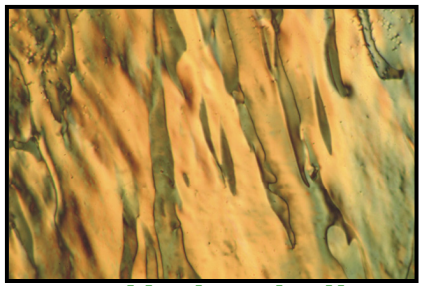
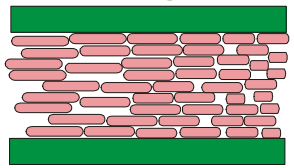


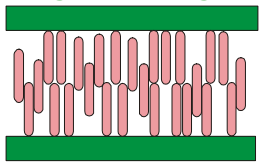


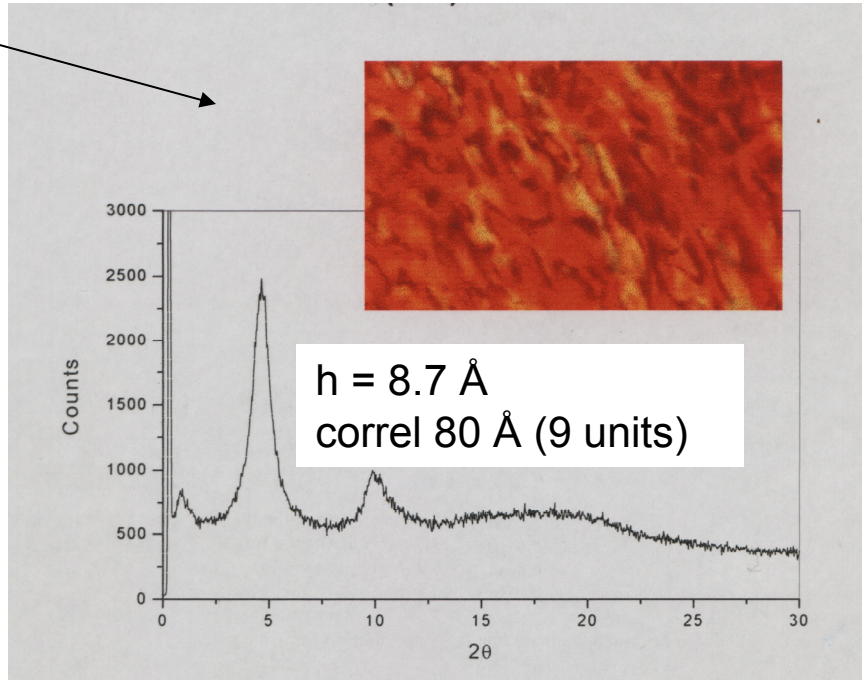
Lipophilic

Hydrophilic



Ncol

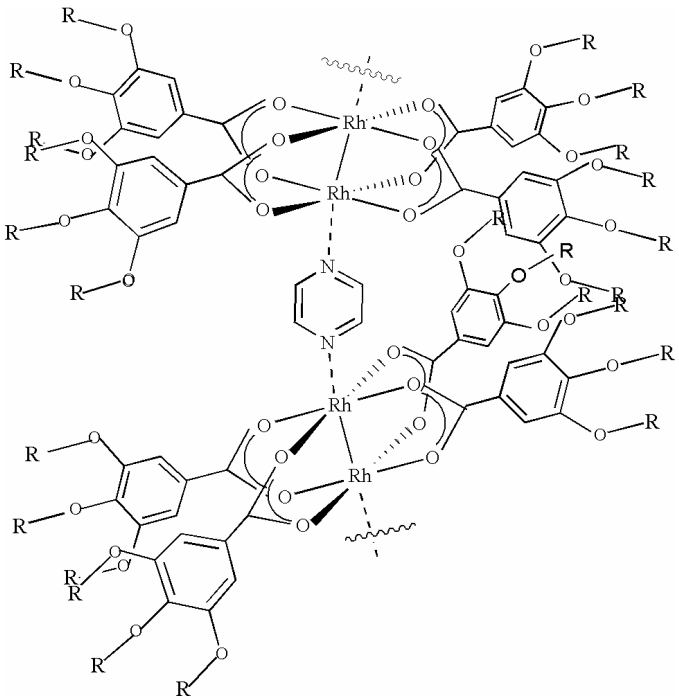




$Rh_2(3,4,5\text{-}B3OCn)_4pz$ series

Experimental h = 7.6 – 8.8 Å

Calculated Σd = 9.7Å



Proposed Model

$Rh_2(3,4,5\text{-}B3OCn)_4pz$ series

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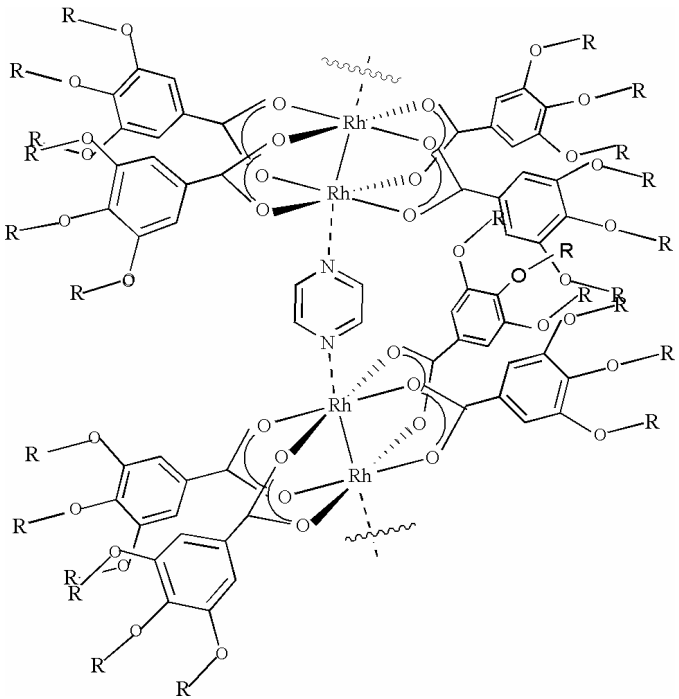
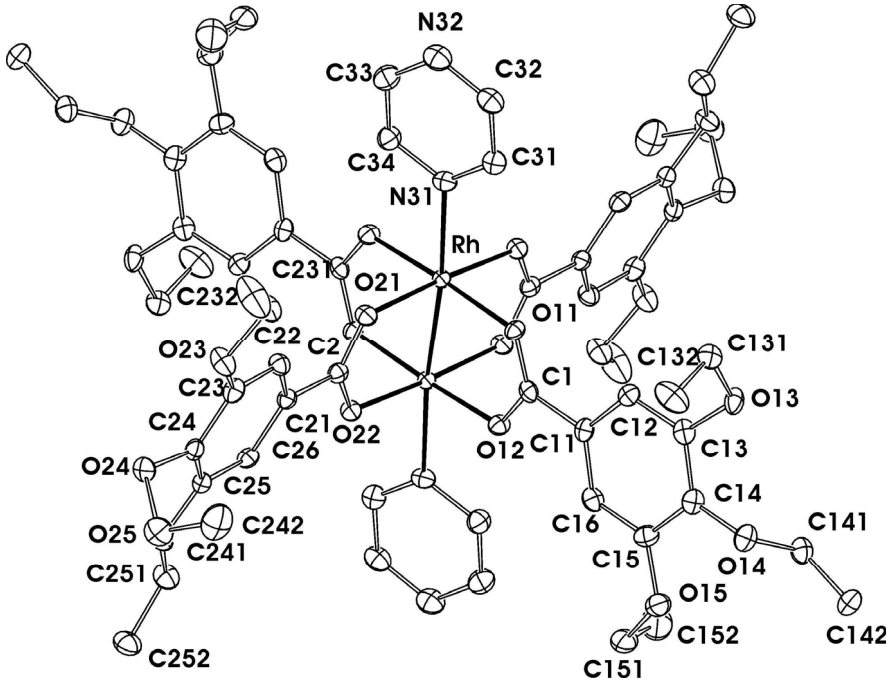


Proposed Model



Crystalline structure of a bis-adduct

(N(31)-Rh-Rh') = 174,57(6)°
(N(32)-N(31)-Rh) = 175,28(6)°
(N(32)-N(31)-Rh-O(21)) = 18,5°

Castro *et al*, *Acta Cryst.* **C58**, m393 (2002)

IV – Chiral centers at $R_{eq}CO_2$: Preliminary results

$Rh_2(3,5\text{-}B2OC9)_4$ $Cr_1 \bullet 107 \bullet Cr_2 \bullet 119 \bullet I$

$Rh_2(3,5\text{-}B2OC18)_4$ $Cr \bullet 45 \bullet Col_H \bullet 90 \bullet I$

$Rh_2(3,5\text{-}B2OC*8)_4$ $Cr \bullet 160 \bullet I$ (racemic $\Rightarrow CH_3$ steric effect))

Role of coordination bonds

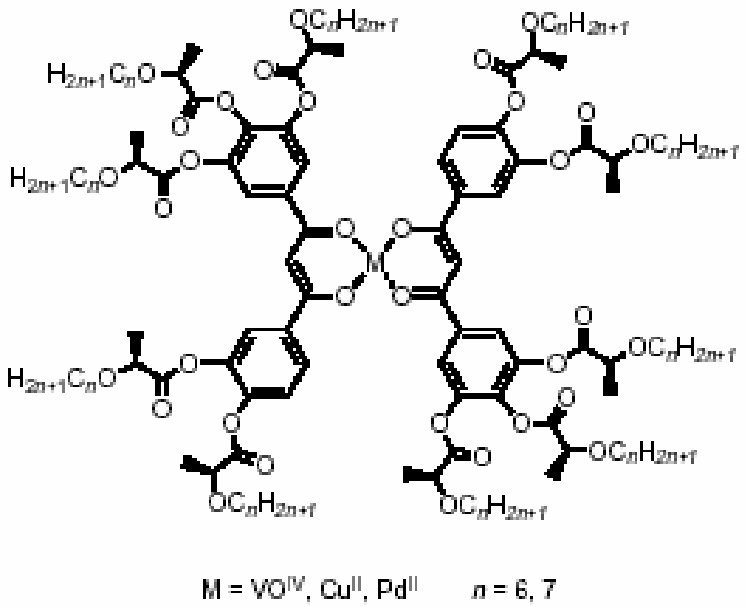
$Rh_2(3,5\text{-}B2OC9)_4pz$ $Cr_1 \bullet 69 \bullet Cr_2 \bullet 110 \bullet Col_N$

$Rh_2(3,5\text{-}B2OC18)_4pz$ $Cr_1 \bullet 57 \bullet Cr_2 \bullet 68 \bullet Col_N \bullet 126 \bullet I$

$Rh_2(3,5\text{-}B2OC*8)_4pz$ $Cr_1 \bullet 90 \bullet Cr_2 \bullet 135 \bullet Col_H \bullet 190 \bullet I$ (racemic)

6th example: Helical columnar metallomesogens based on square-planar β-diketones

Helical columnar metallomesogens with the chiral center at the aliphatic chains



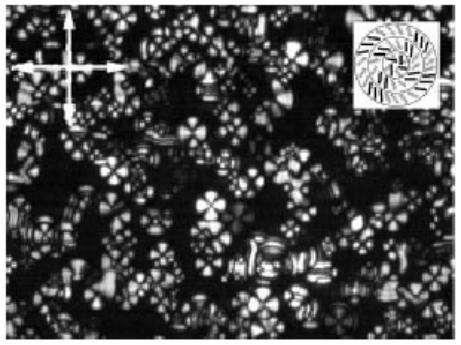
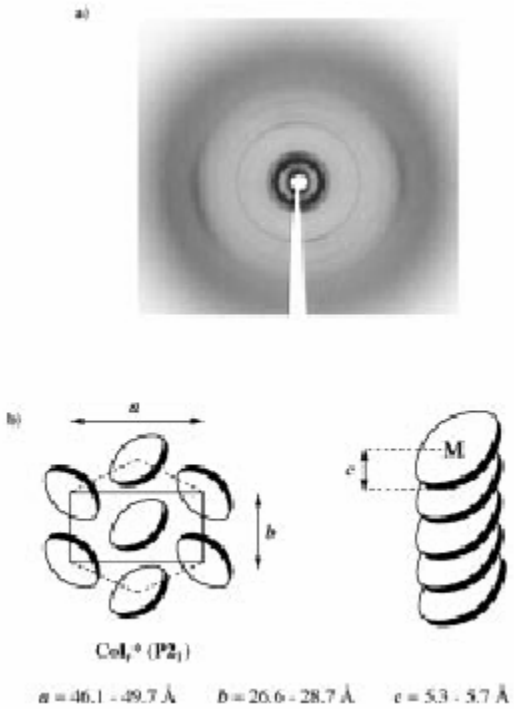


Figure 4. Photomicrograph of the texture of the annealed (100 °C for 20 h) columnar mesophase of compound **dK"7"VO**. The texture shows Maltese crosses inclined with respect to the crossed polarizers indicating the presence of molecular tilt as represented in the figure at the top righthand corner of the picture.



Serrano, Sierra, *Chem Eur J* **6**, 759 (2000)

Stereoch. Aspects of Metallomesogens – Ex # 6 (Helicity by chiral ligands)

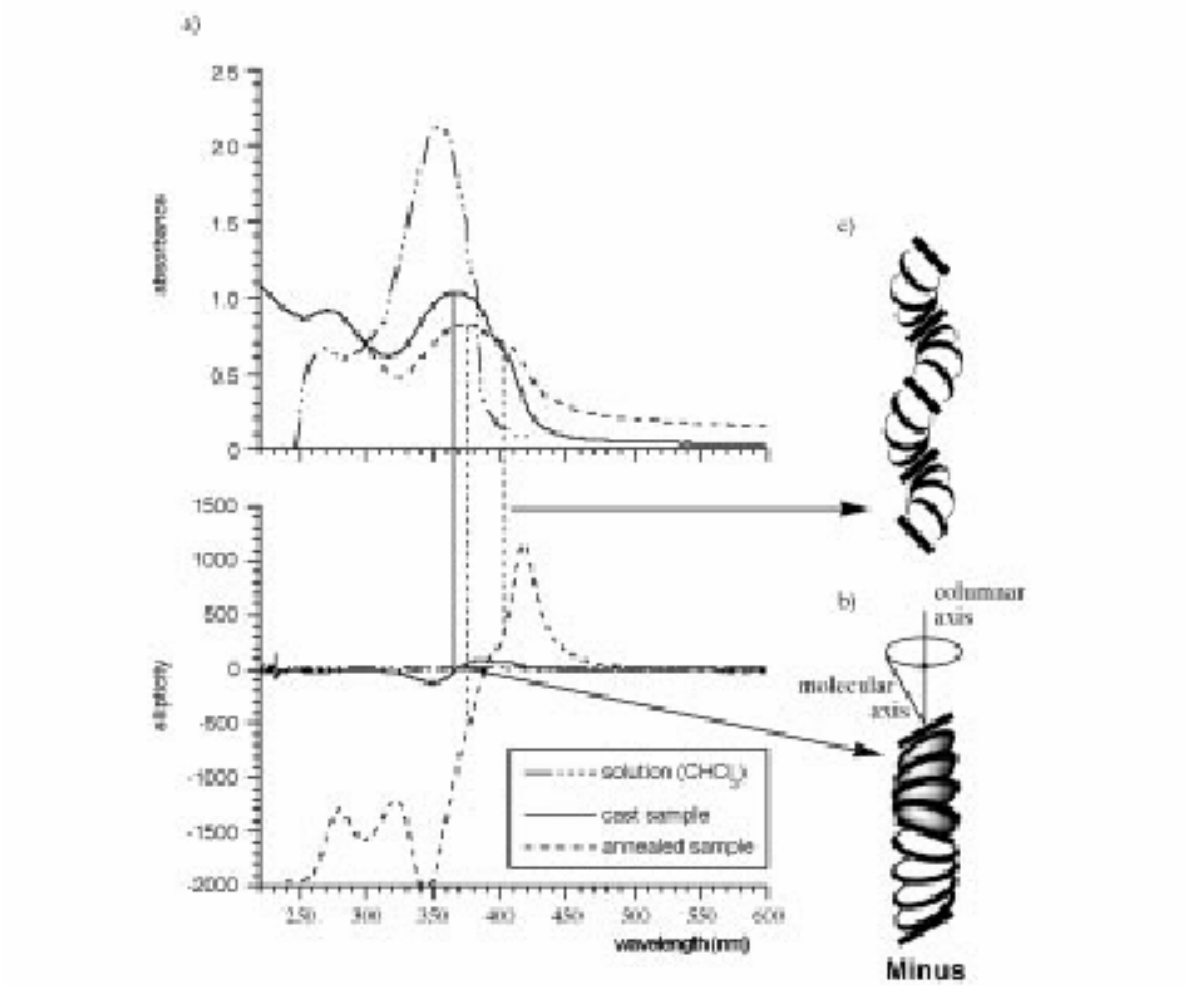
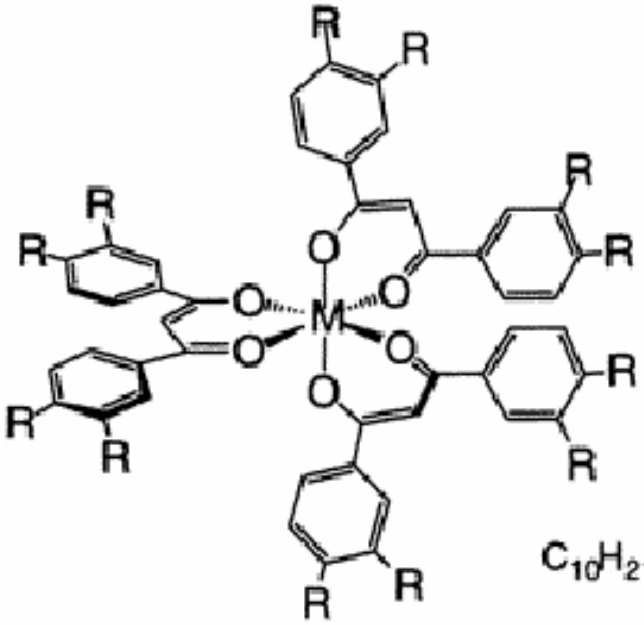


Figure 6. a) UV and CD spectra recorded for complex **dK"7"VO** under three different conditions: solution in THF (0.1 gL^{-1}) and thin film deposited on a quartz substrate by spin coating (cast sample and annealed sample, 100 °C for 20 h). b, c) The structures of the proposed helical arrangements are represented related with the appearance of exciton-splitting signals.

7th example: Helical columnar metallomesogens based on octahedral β-diketones

Chirality at the metal center: spontaneous resolution of Δ and Λ domains in columnar systems

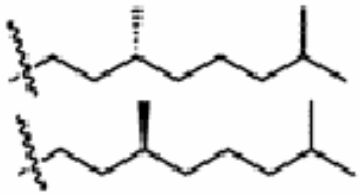
Swager *et al*, *J. Am. Chem. Soc.* **121**, 4518 (1999).



Metal	Chain	Phase sequence	
Fe(III)	$C_{12}H_{25}$	**Col_H** 91ºC **Col_H** 111ºC **I**	fluxional
Mn(III)	$C_{12}H_{25}$	**Col_H** 62ºC **Col_H** 107ºC **I**	fluxional
Co(III)	$C_{12}H_{25}$	**Col_R** 61ºC **Col_H** 104ºC **I**	locked
Cr(III)	$C_{12}H_{25}$	**Col_R** 65ºC **Col_H** 108ºC **I**	locked

$C_{10}H_{21}$*= R-dihydrocitronellyl

S-dihydrocitronellyl

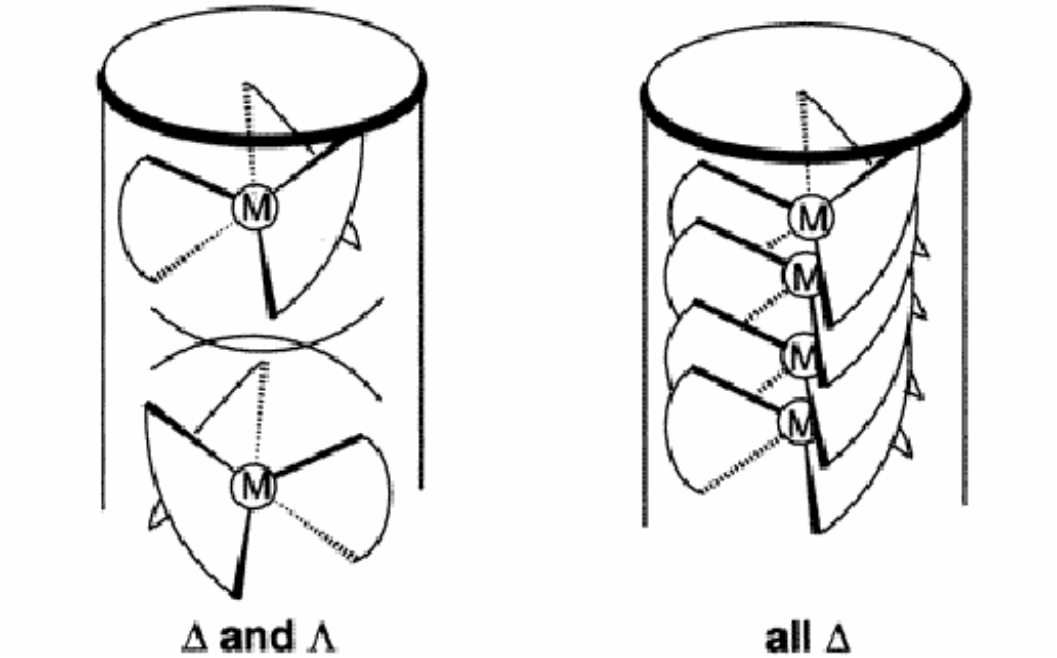


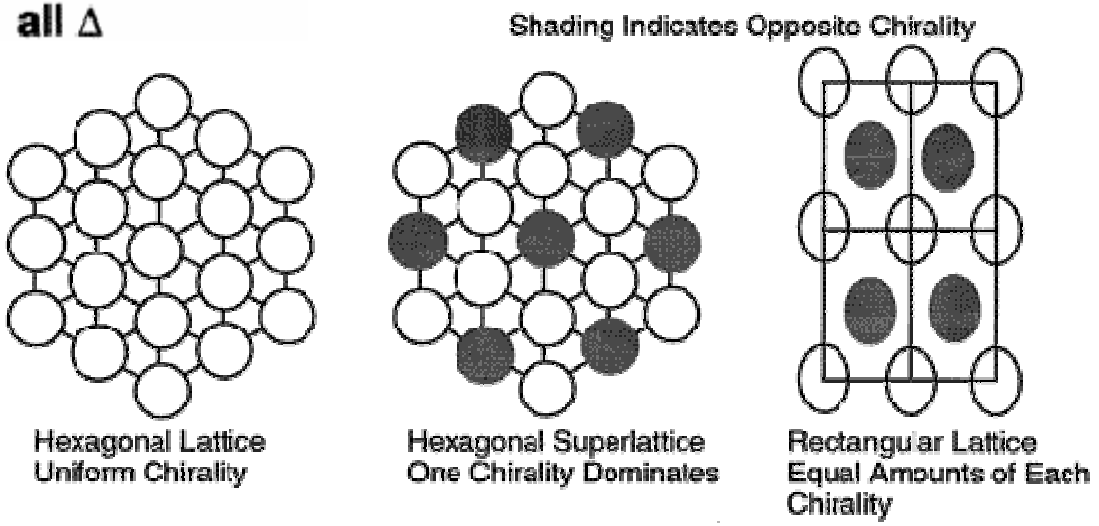
Stereoch. Aspects of Metallomesogens – Ex # 7 (Helicity by chirality at M)

... Crystal field activation energies (in *Dq*) for dissociation mechanism
Octahedral → square pyramid

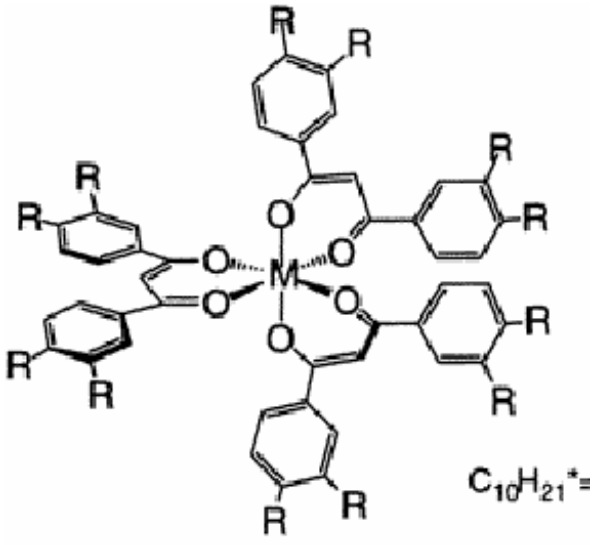
System	Strong Fields			Weak Fields		
	Octahedral	Square Pyramid	C.F.A.E.	Octahedral	Square Pyramid	C.F.A.E.
d^0	0	0	0	0	0	0
d^1	4	4.57	−0.57	4	4.57	−0.57
d^2	8	9.14	−1.14	8	9.14	−1.14
d^3	12	10.00	2.00	12	10.00	2.00
d^4	16	14.57	1.43	6	9.14	−3.14
d^5	20	19.14	0.86	0	0	0
d^6	24	20.00	4.00	4	4.57	−0.57
d^7	18	19.14	−1.14	8	9.14	−1.14
d^8	12	10.00	2.00	12	10.00	2.00
d^9	6	9.14	−3.14	6	9.14	−3.14
d^{10}	0	0	0	0	0	0

Stereoch. Aspects of Metallomesogens – Ex # 7 (Helicity by chirality at M)



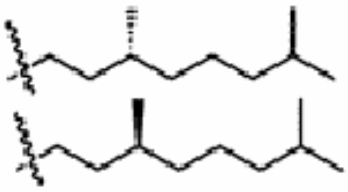


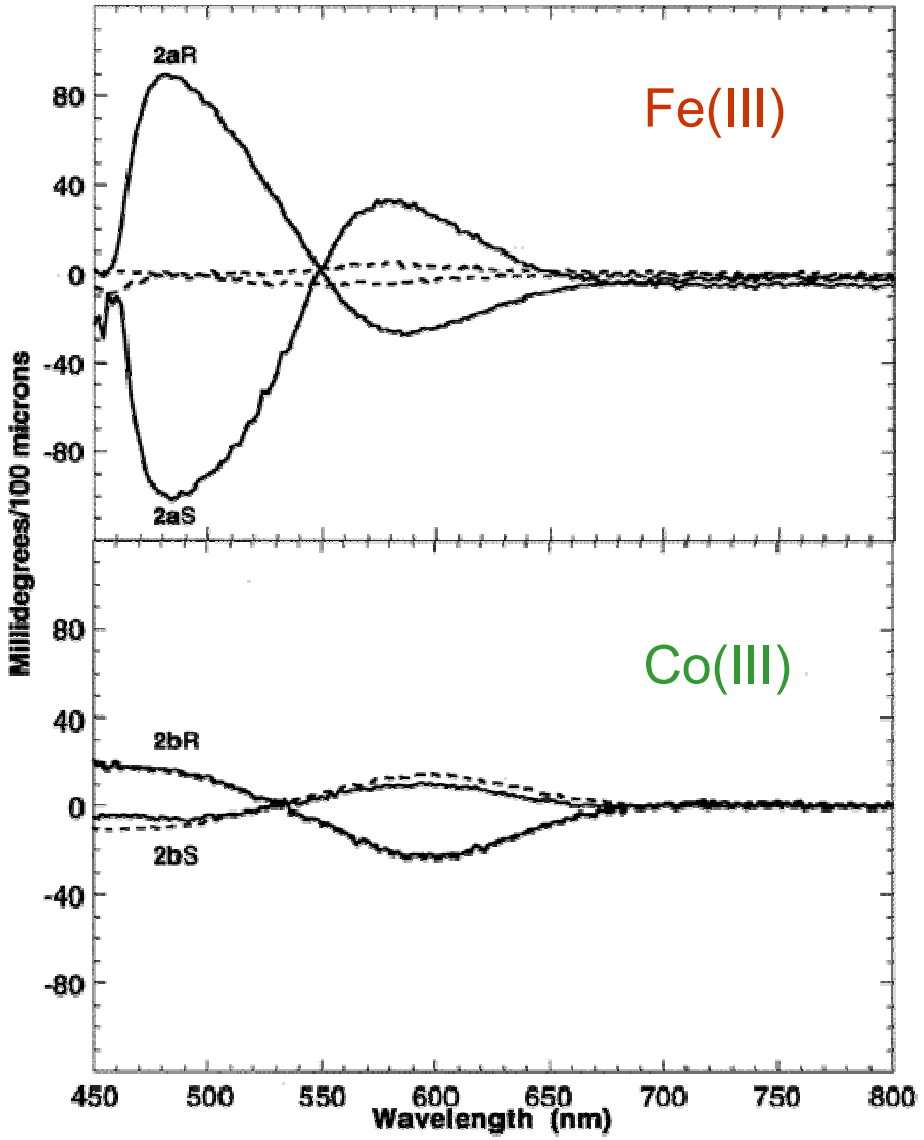
Stereoch. Aspects of Metallomesogens – Ex # 7 (Helicity by chirality at M)



$C_{10}H_{21}$*= R-dihydrocitronellyl

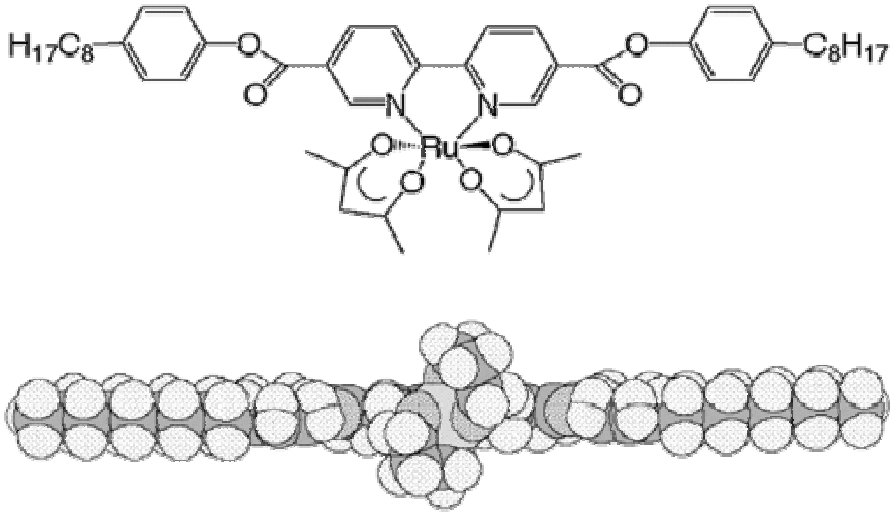
S-dihydrocitronellyl



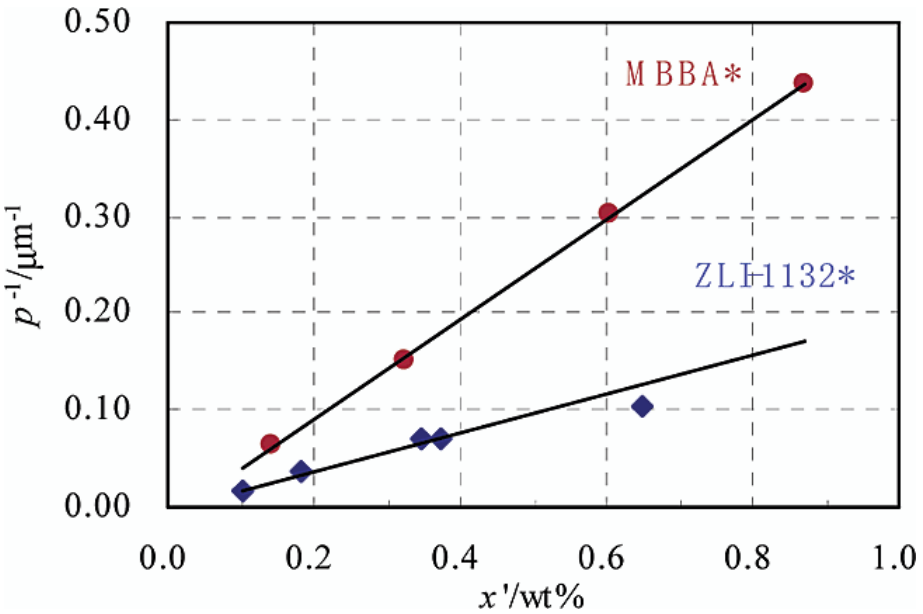


8th example: Chiral dopants for nematics based on octahedral β-diketones

Chirality at the metal center: Large Helical Twisting Power for Δ-[Ru(acac)$_2$L] calamitic dopant for NLC



Hoshino *et al*, *J. Am. Chem. Soc.* **125**, 1718 (2003).



Plots of the inverse helical pitch (p^{-1}) versus weight percentage of the dopant (x') for solutions of Δ-[Ru(acac)$_2$L] in ZLI-1132 and MBBA.

Stereochemical (at M) and regiochemical (at L) control of HTP in nematics

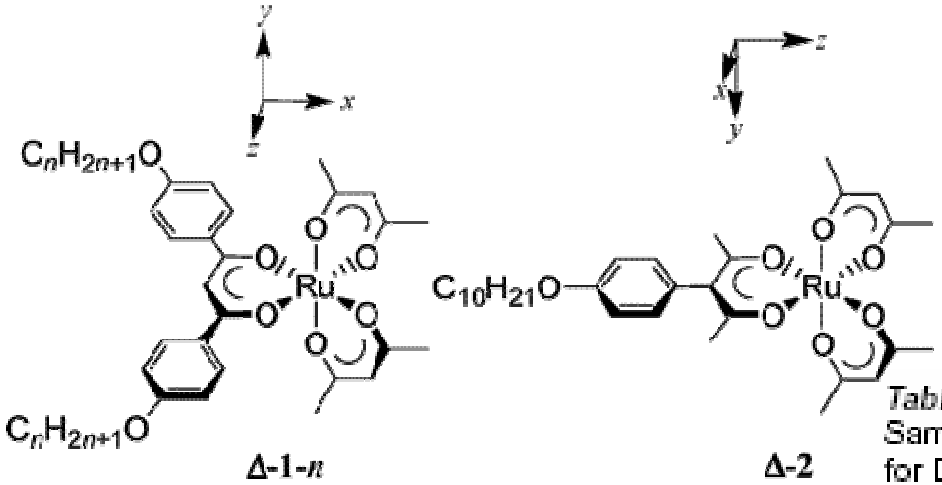


Table 1. Values for the HTP (β_M)[a] Evaluated for the Enantiomeric Samples of Ru(III) Complexes and the ICD Spectral Data (θ/deg)[b] for Doped N* Phases

	β_M/μm^{-1}				θ/deg			
dopant	Δ	Λ	host[c]	T/°C	Δ	Λ	λ/nm	p/μm
1-6	−146	130	MBBA	30	−0.83	1.05	420	5.1
1-12	−127	120	MBBA	30	−0.78	0.59	420	8.3
	−66	72	EBBA	60	−0.69	0.88	420	7.5
	−55	58	ZLI-1132	35	−1.00	1.07	330	17
	−63[d]	39[d]	PAA	120	−1.34	1.33	480	7.2
2	24	−25	MBBA	30	0.13	−0.16	420	14
	16	−13	EBBA	60	0.55	−0.41	420	13
	24	−22	ZLI-1132	35	0.22	−0.28	330	24
	17	−13[d]	PAA	120	0.25	−0.37	480	15

[a] The signs + and − indicate that *P*- and *M*-helical superstructures are induced, respectively. [b] Ellipticity readings taken at band edges of the ICD spectra, which are exemplified in Figure 2. Concentrations of the listed samples with Δ- and Λ-enantiomers are not exactly matched, and the mean helical pitch length is given for each pair, for comparison to the specified wavelength (λ/nm). [c] Abbreviations and experimental nematic ranges: *N*-(4-methoxybenzylidene)-4-*n*-butylaniline (MBBA, 21−47 °C), *N*-(4-ethoxybenzylidene)-4-*n*-butylaniline (EBBA, 36−73 °C), and 4,4′-azoxydianisole (PAA, 118−135 °C). ZLI-1132 is a mixture of 4-(4-alkylcyclohexyl)benzonitrile and 4-(4-alkylcyclohexyl)-4′-cyanobiphenyl derivatives (Merck Japan, T_{NI} = 72.3 °C, average mw = 263.2). [d] Rough estimates from finite concentrations within a range of *x* = 0.14−0.18 mol %.

Stereoch. Aspects of Metallomesogens – Ex # 8 (chirality at M and HTP)

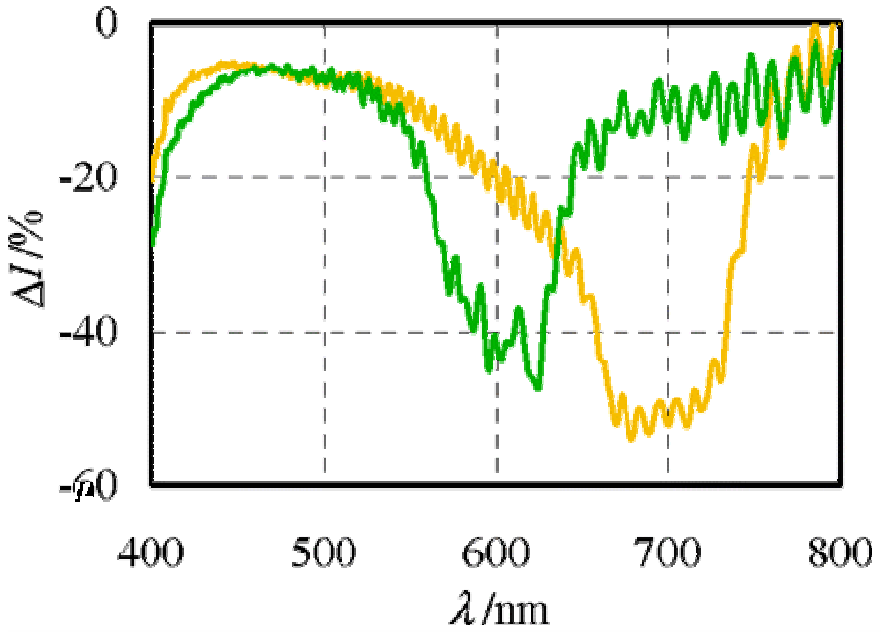
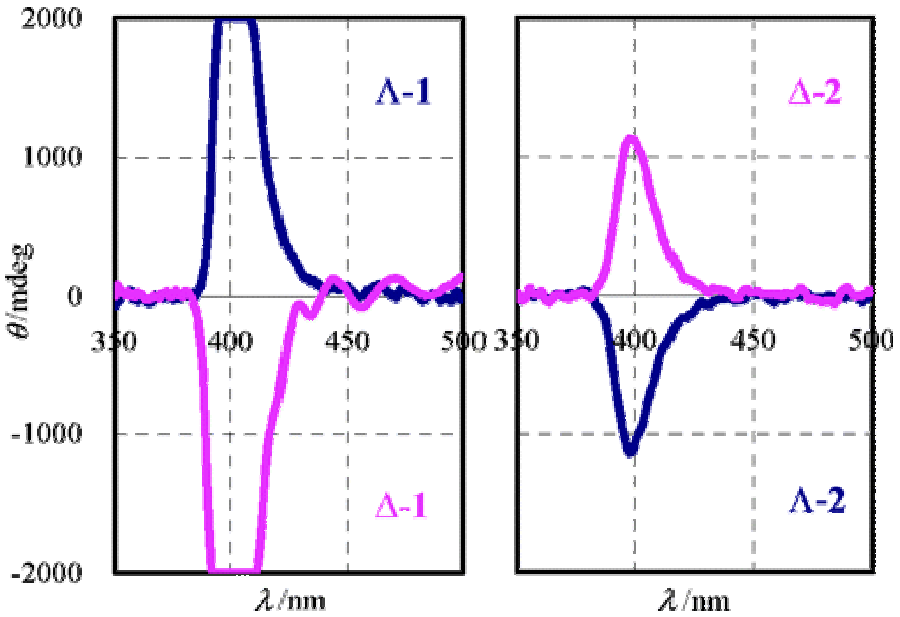


Figure 4. "Difference" transmittance (ΔI) spectra for MBBA* materials doped with Δ-**1**-12 (1.9 and 2.2 mol % for yellow and green spectra, respectively), showing dips due to the selective reflection in the N* state. The original spectra were measured at 20 °C in glass cells of 25-μm gap at normal incidence.

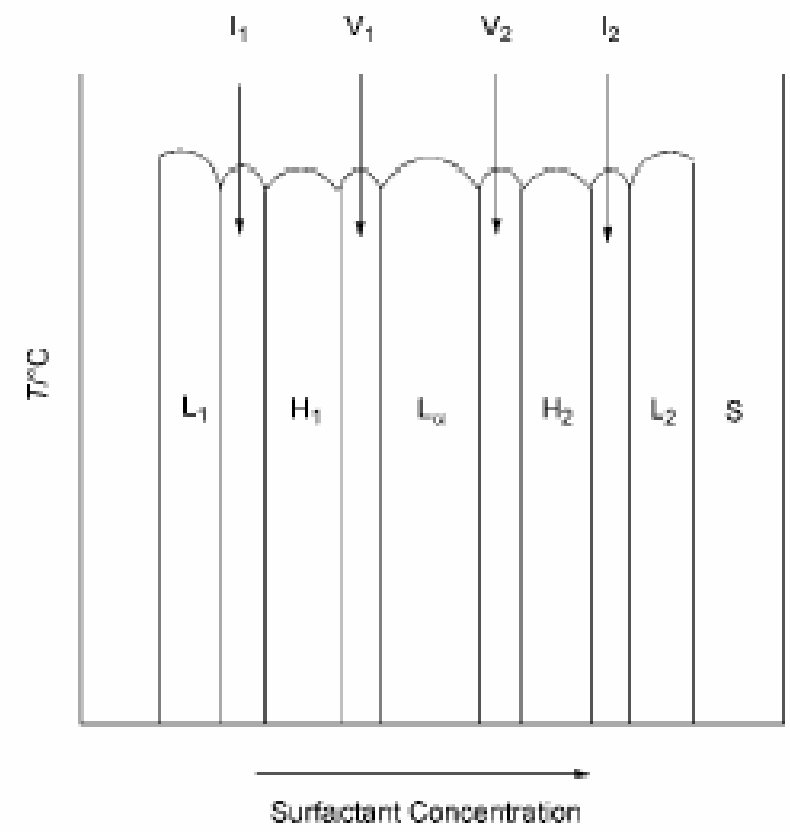


ICD spectra for MBBA* materials doped with Δ- and Λ-enantiomers of **1**-12 (0.1 mol %, left) and **2** (0.3 mol %, right). Each spectrum was recorded at 30° C in a glass cell of 25-μm gap at normal incidence.

Hoshino *et al*, *J. Am. Chem. Soc.* **127**, 8453 (2005).

9th example: Cubic phases in poycatenar metallomesogens

Key factors in Cub phases occurence



Lyotropics – Thermotropics analogy

Lα : Calamitic S

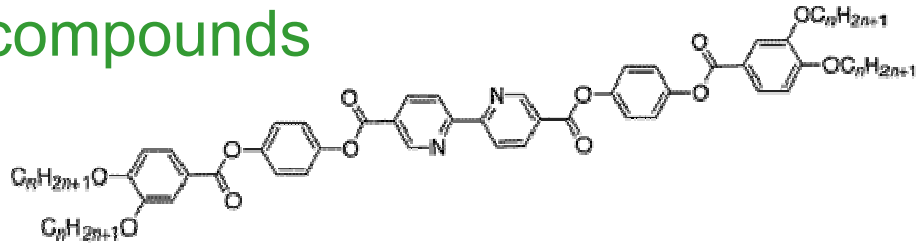
H_2 : Discotic columnar

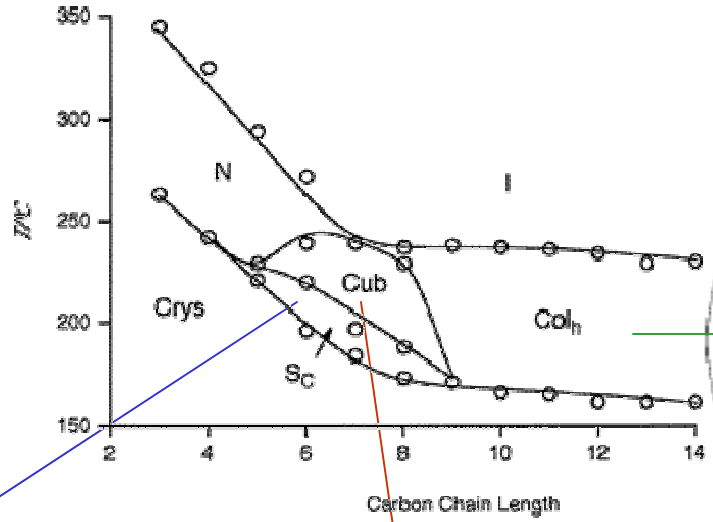
V_2: Bicontinous cubic ?

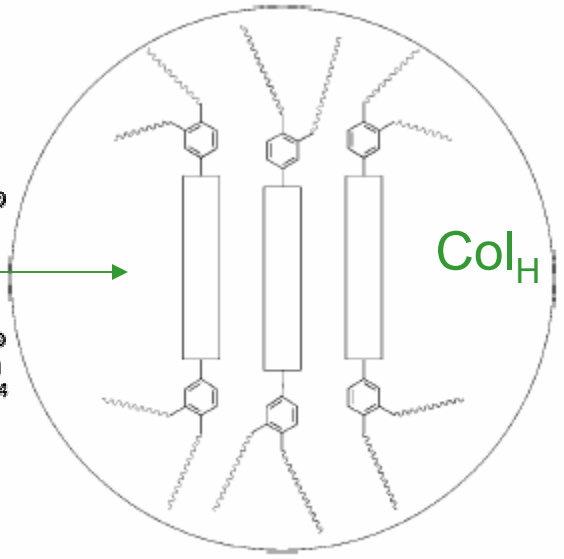
I_2: Micellar cubic ?

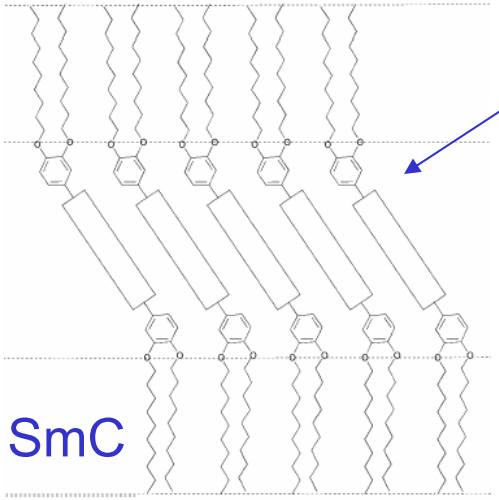
Bruce, Guillon et al, *J. Mater. Chem* **11**, 2852 (2001)

Polycatenar compounds







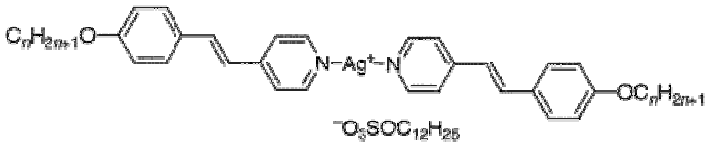


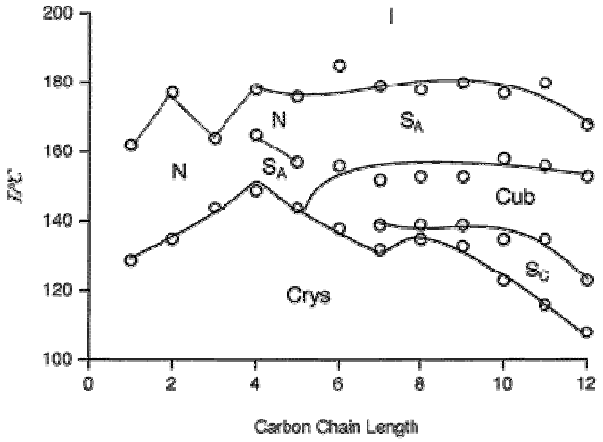
Cub

Also aggregation behaviour?

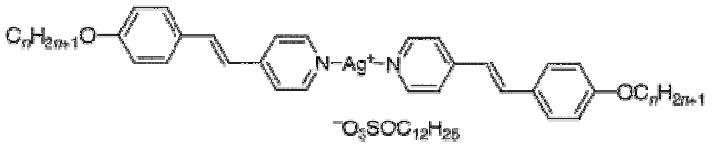
Broken lamellae with aggregation

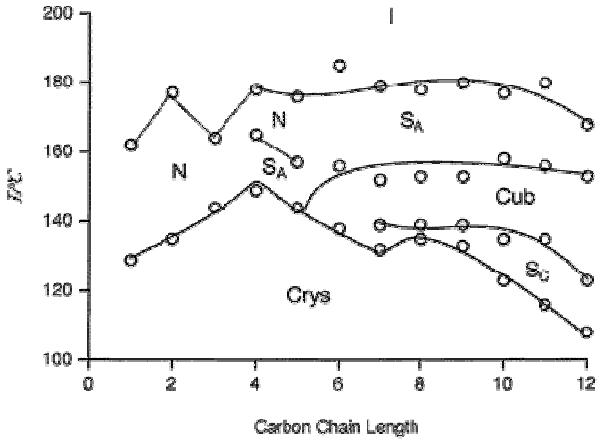
Polycatenar sylver metallomesogens



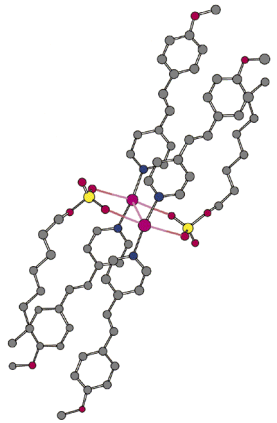


Polycatenar sylver metallomesogens

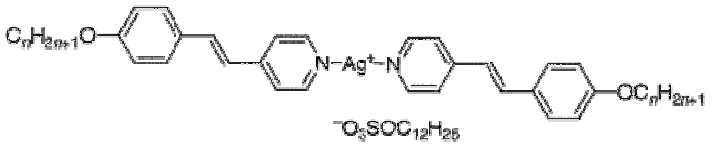


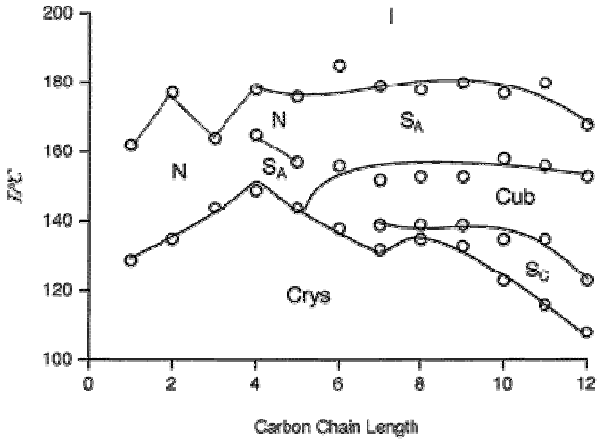


N: not "ionic"



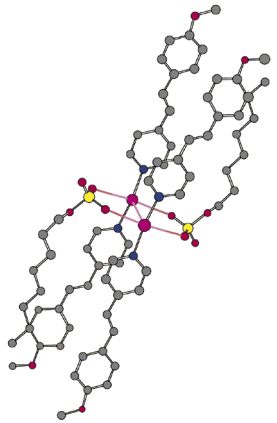
Polycatenar sylver metallomesogens



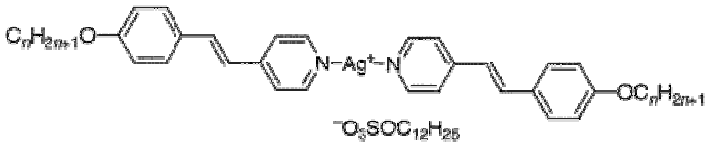


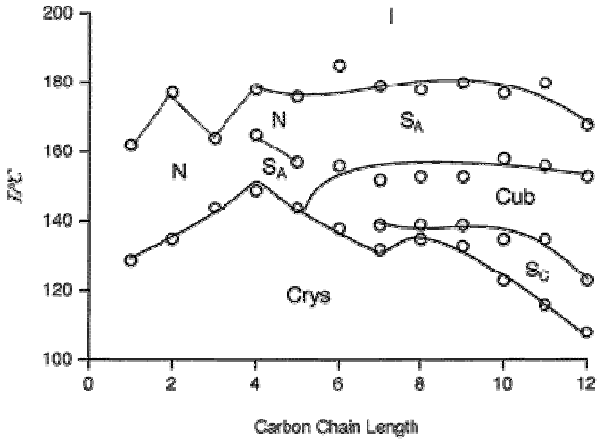
N: not "ionic"

Calamitic with lateral chains ⇒ N, not S !



Polycatenar sylver metallomesogens

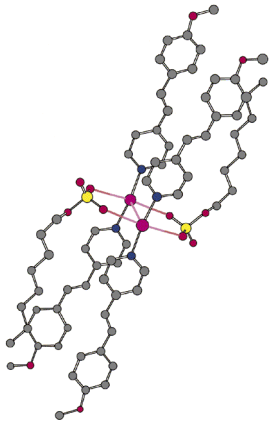




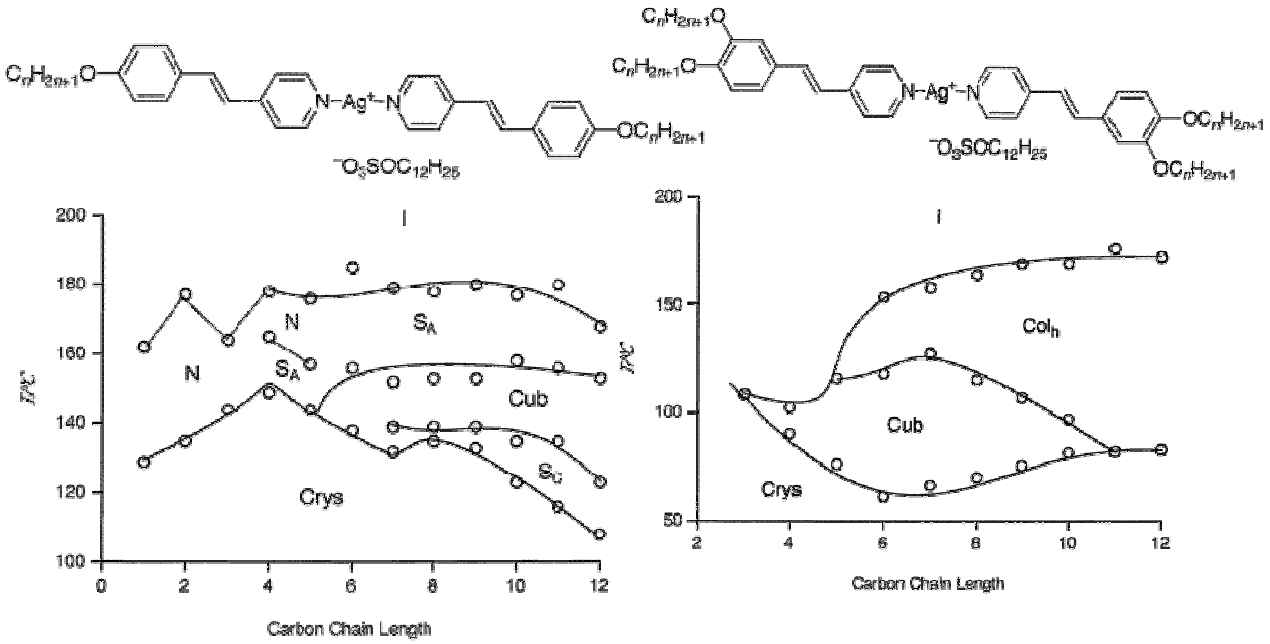
N: not "ionic"

Calamitic with lateral chains ⇒ N, not S !

Cub: with DOS bot not with OS



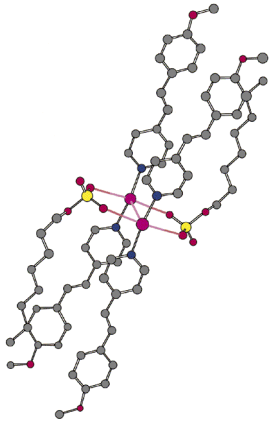
Polycatenar sylver metallomesogens



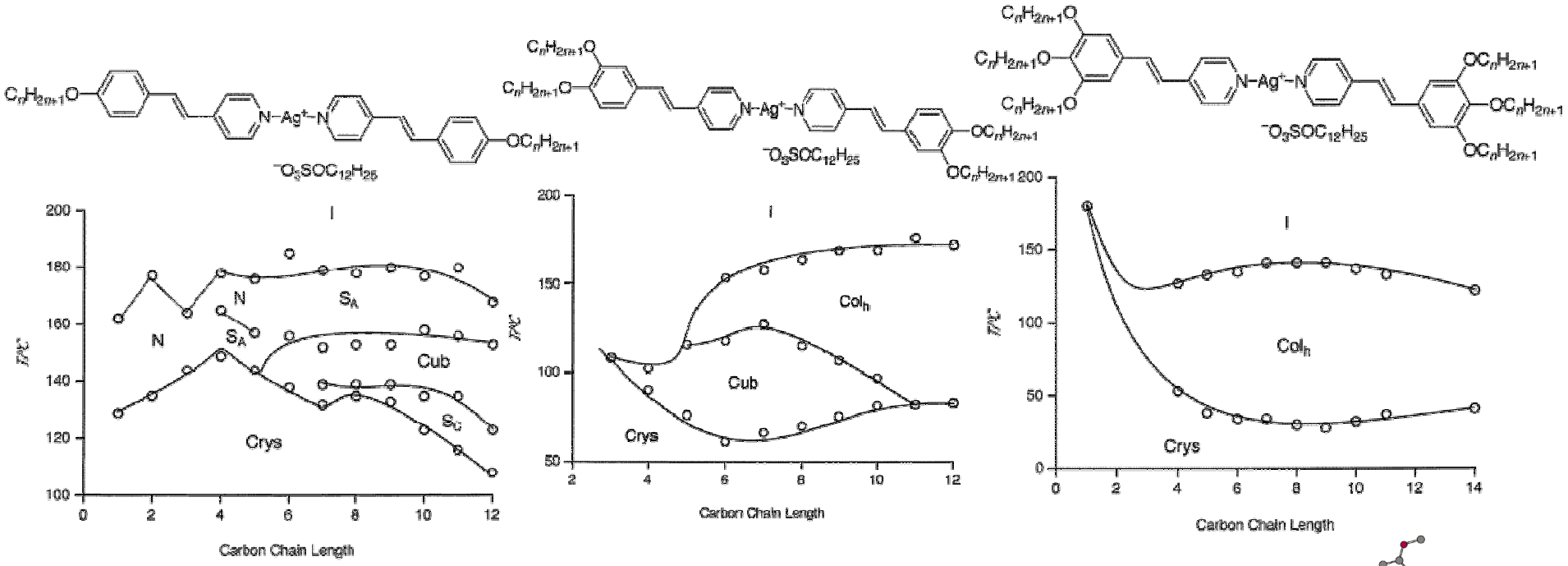
N: not "ionic"

Calamitic with lateral chains ⇒ N, not S !

Cub: with DOS bot not with OS



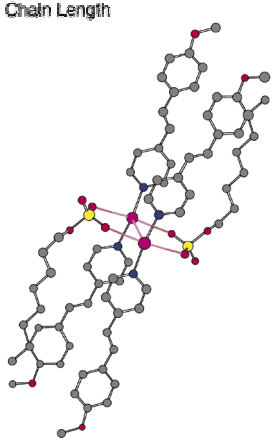
Polycatenar sylver metallomesogens



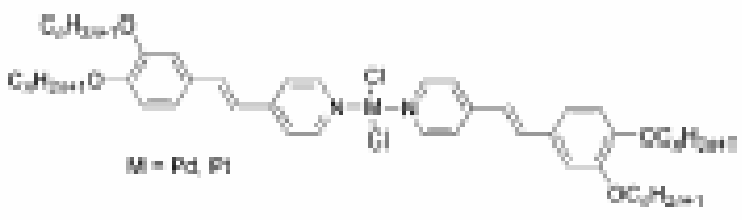
N: not "ionic"

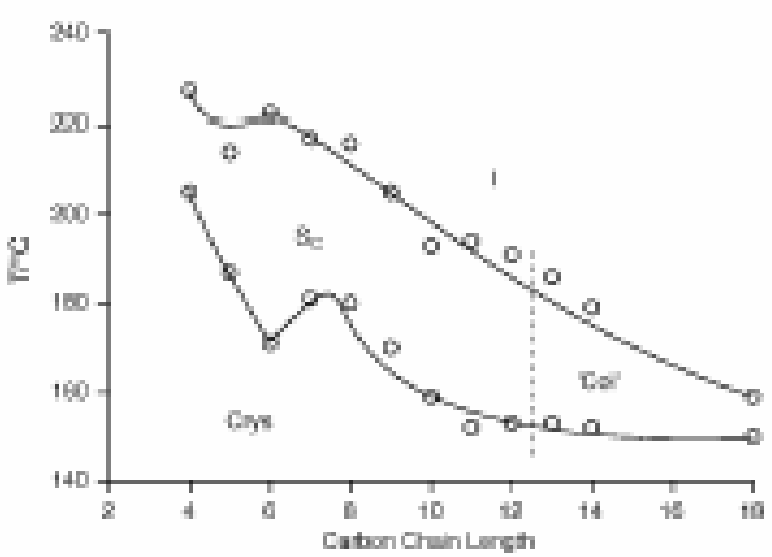
Calamitic with lateral chains ⇒ N, not S !

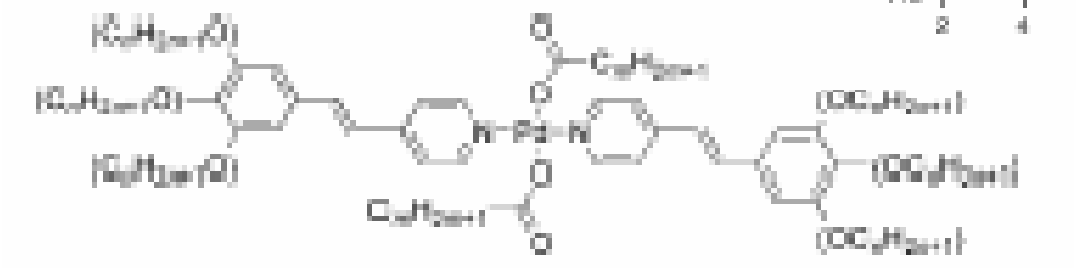
Cub: with DOS bot not with OS



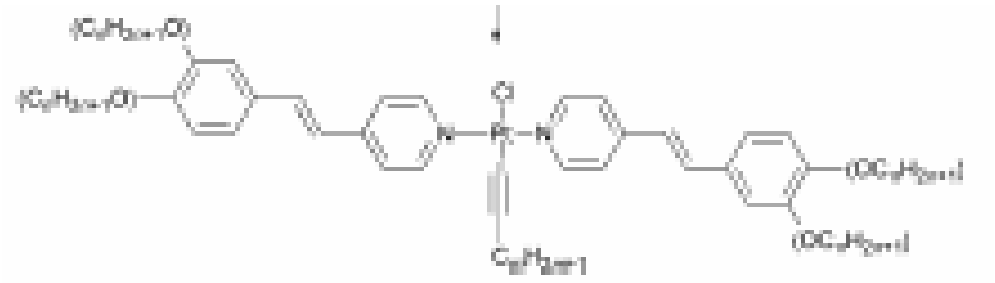
Pt and Pd polycatenars







All N (also N_D?)



N, Sc (not Cub)

Stereoch. Aspects of Metallomesogens – Ex # 9 (Cubics in polycatenars)

Acetylide, DOS: similar length, ≠ M-L electrostatic character

DOS, OS: similar M-L electrostatic character, ≠ length

Both interactions and microsegregation play a role in ***Cub*** *formation*

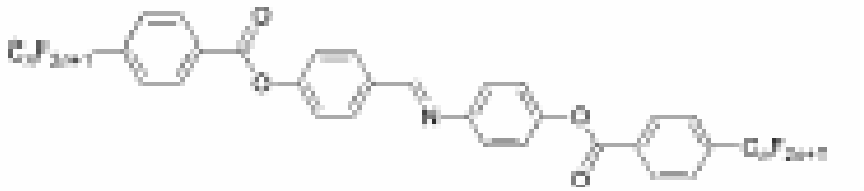
Stereoch. Aspects of Metallomesogens – Ex # 9 (Cubics in polycatenars)

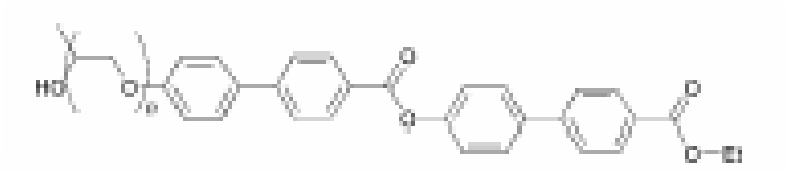
Acetylide, DOS: similar length, ≠ M-L electrostatic character

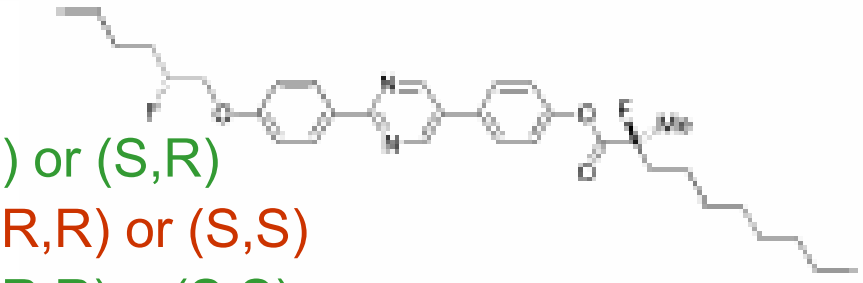
DOS, OS: similar M-L electrostatic character, ≠ length

Both interactions and microsegregation play a role in ***Cub*** *formation*

Specific interactions in ***Cub*** *formation*



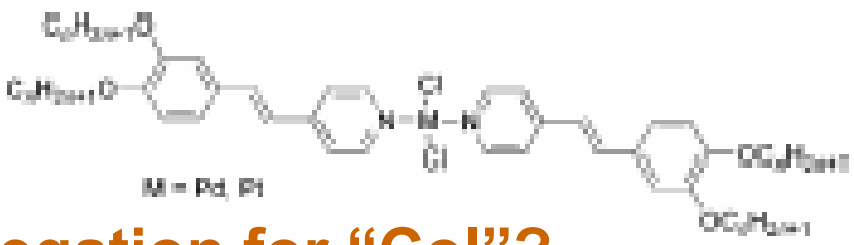




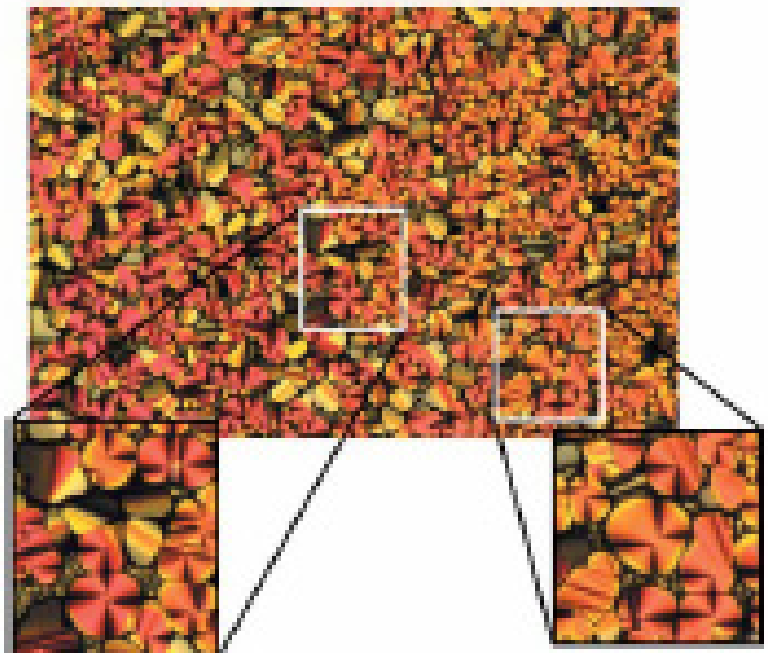
(R,S) or (S,R)
not (R,R) or (S,S)
but (R,R) + (S,S)

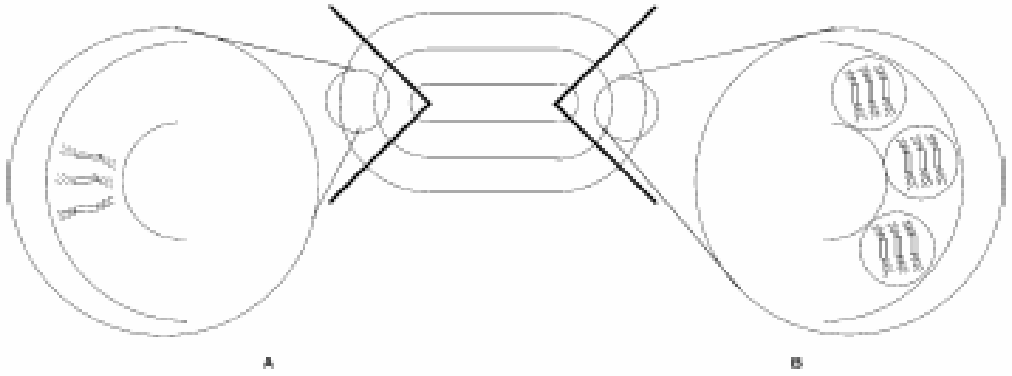
Aggregation

Why



did not exhibit Cub but aggregation for "Col"?





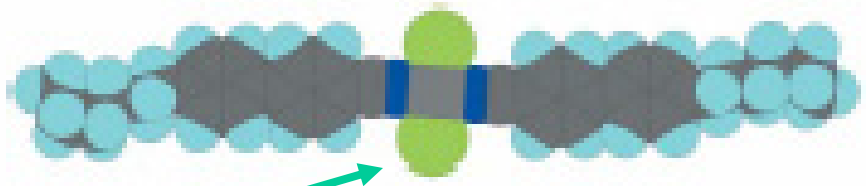
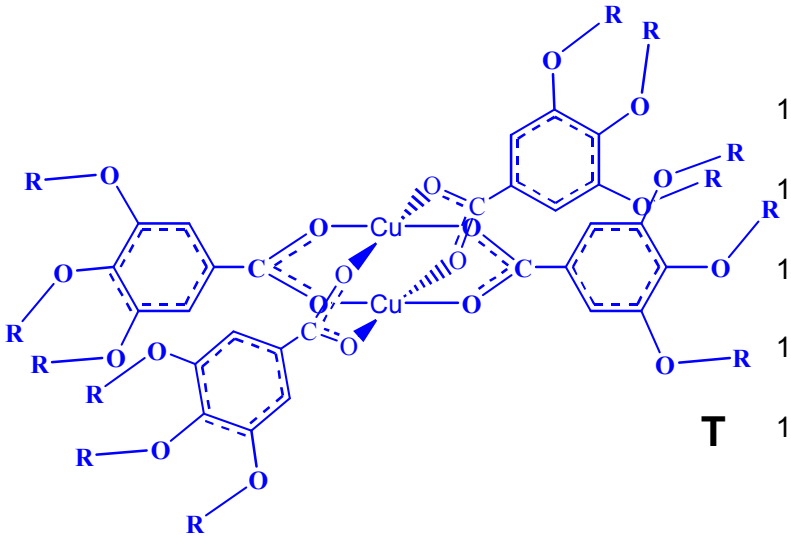


Fig. 25 Space-filling representation of the molecular structure of *trans*-[PtCl$_2$(py)$_2$(B$_{12}$)]

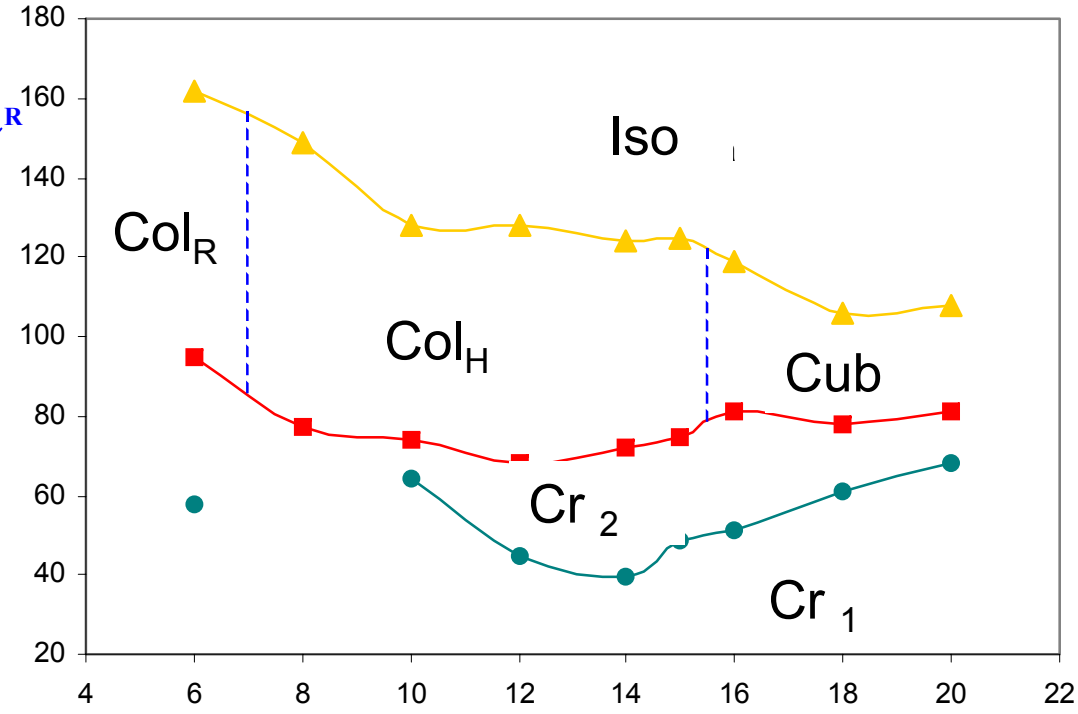
"Bulky" Cl avoids aggregation

10th example: Cubic mesophases in copper derivatives of B3OCn ligands

Unexpected way of "aggregation"

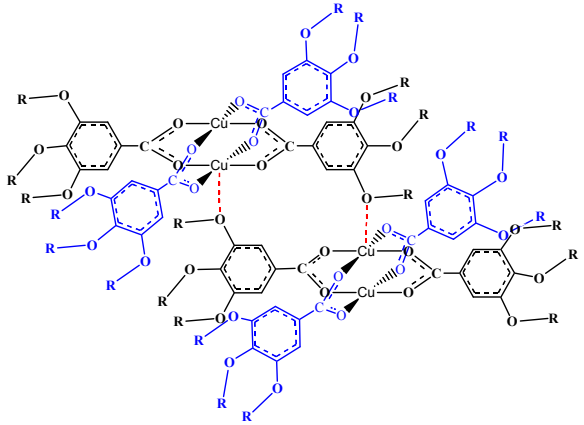


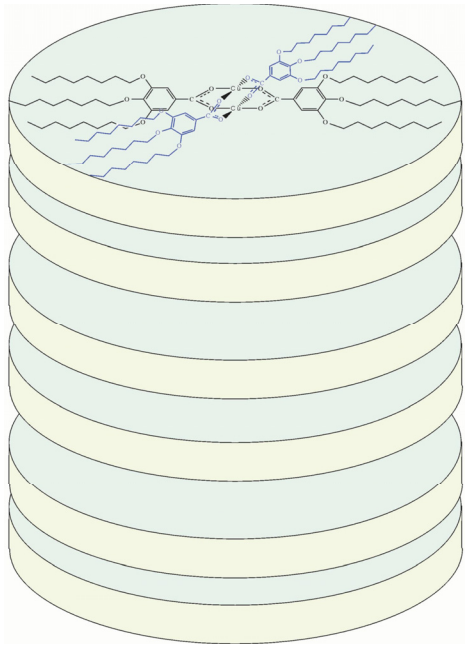
T



Chaia, Guillon et al, *Mol. Cryst. Liq. Cryst.*, 330, 213 (1999)

Stereoch. Aspects of Metallomesogens – Ex. #10 (Cub in $Cu_2(B3OCn)_4$)





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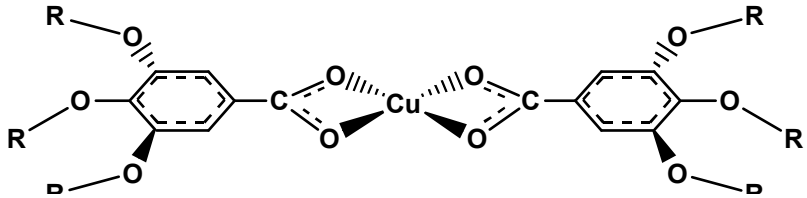

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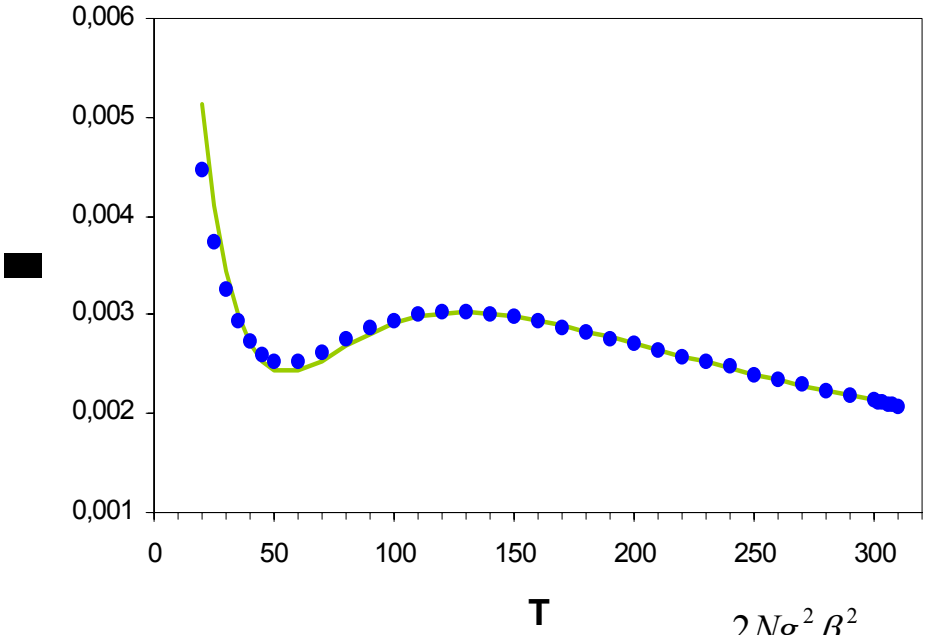

$$\chi_{dímero} = (1-p)\chi' + p\frac{Ng_{mo}{}^2\beta^2}{2kT}$$

$$\chi' = \frac{2Ng^2\beta^2}{kT\left[3+\exp^{\frac{-J}{kT}}\right]}$$

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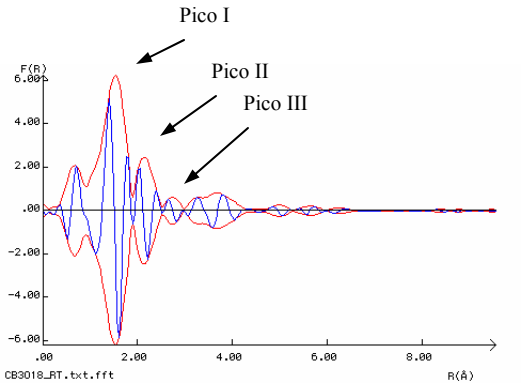
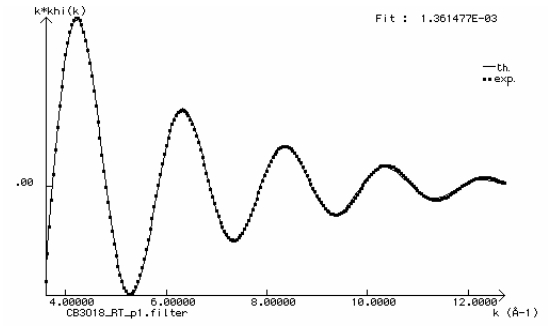
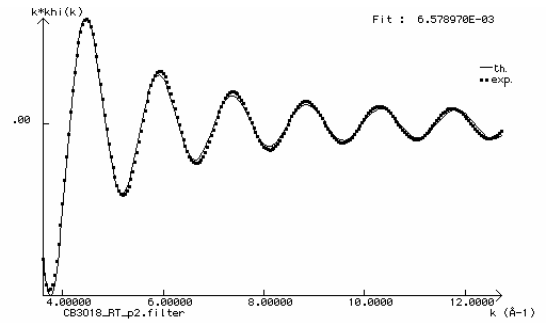
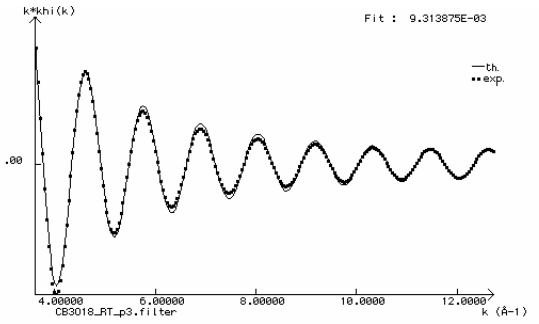
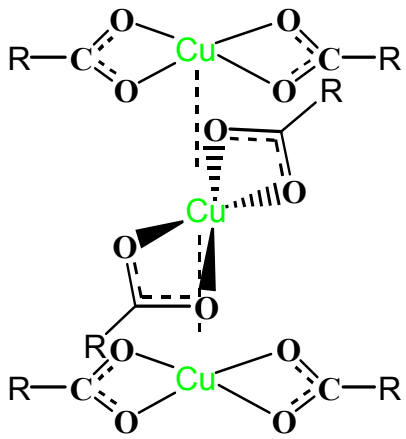
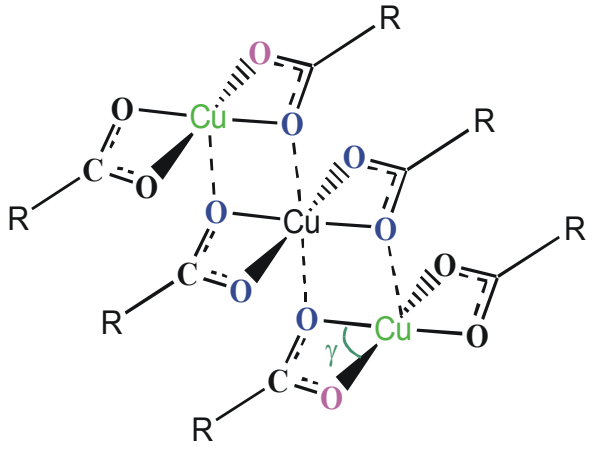




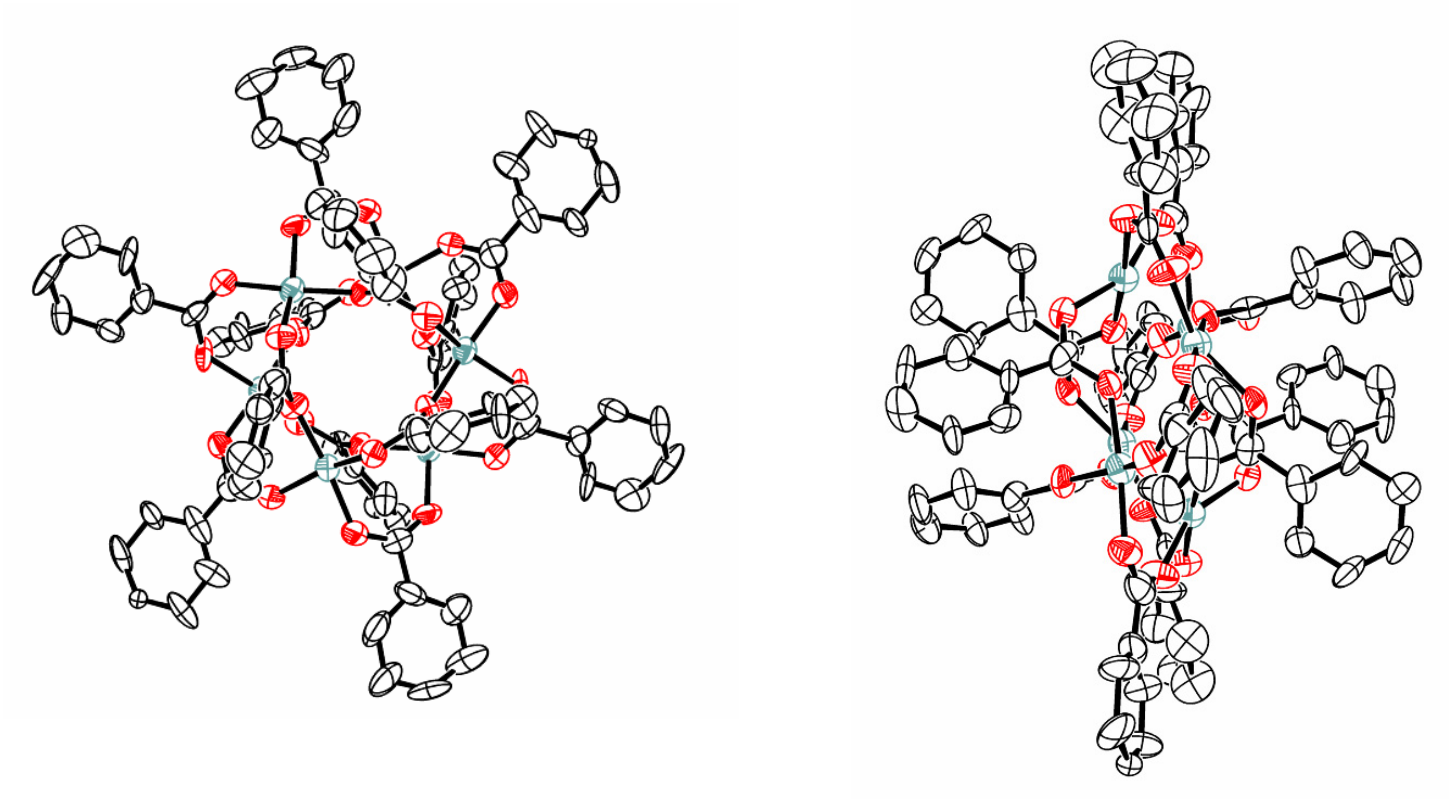








Crystalline Structure of the B3OC2 derivative



Hexameric "globular" molecular units!

Vega *et al Acta. Cryst.* (2005, sent)

Stereochemical aspects of Metallomesogens: Final Comments

Metallomesogens: a promise or a fact?

R. Giménez, D.P. Lydon, J.L. Serrano*

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Received 15 November 2002; received in revised form 18 February 2003; accepted 20 February 2003

An analysis of the reports from the last few years leads to a conclusion concerning the applications of metallomesogens: the promising potential has so far exceeded the actual results.

Generally, the presence of the metal in the compounds does not favour application in liquid crystal displays because, in most cases, an important increase in the conductivity of the materials with respect to the traditional organic compounds is observed. The high viscosity of metallomesogens is responsible for the high electric fields applied. Under these conditions, the metal–ligand bond is quite labile and causes the increase in conductivity.

The orientation of the materials under magnetic fields is referenced in many papers as a potential application for metallomesogens. However, the requirement for high fields prevents this method from being useful.

In some other cases, like the applications cited for lanthanide-containing metallomesogens or metallocycles, the final properties depend only on the structure of the compounds and the liquid crystallinity is not essential.

Some results with metallomesogenic polymers seem promising; however, no practical applications have yet been described.

In spite of these arguments, an important variety of new structures has been described in the last few years, inconceivable with purely organic compounds. This demonstrates the enormous potential of metallomesogens as a 'testing bench' for structure–activity studies. Proof of this is the appearance of the McMillan phase in a mixture of metallomesogens and TNF.

The formation of well-ordered supramolecular assemblies of macroscopic dimensions, such as metallohelicates or some metal-containing liquid crystals capable of aggregation as supramolecular helical structures opens up new perspectives in materials science.

Finally, in the case of lyotropic metallomesogens, the use of transition metal-containing surfactants or non-ionic surfactants capable of interacting with salts of these metals as templates has provided a method to obtain nano- and meso-structures of short-term application for catalysis.

In conclusion, metallomesogens continue to be promising compounds in materials science.

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Orientation under magnetic fields: requirement for high fields prevents this method to be used

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Applications for lanthanide metallomesogens: depend only on the structure of the compounds and LC is not essential

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Enormous potential as “testing-bench” for structure-activity studies

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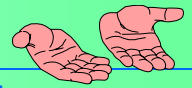
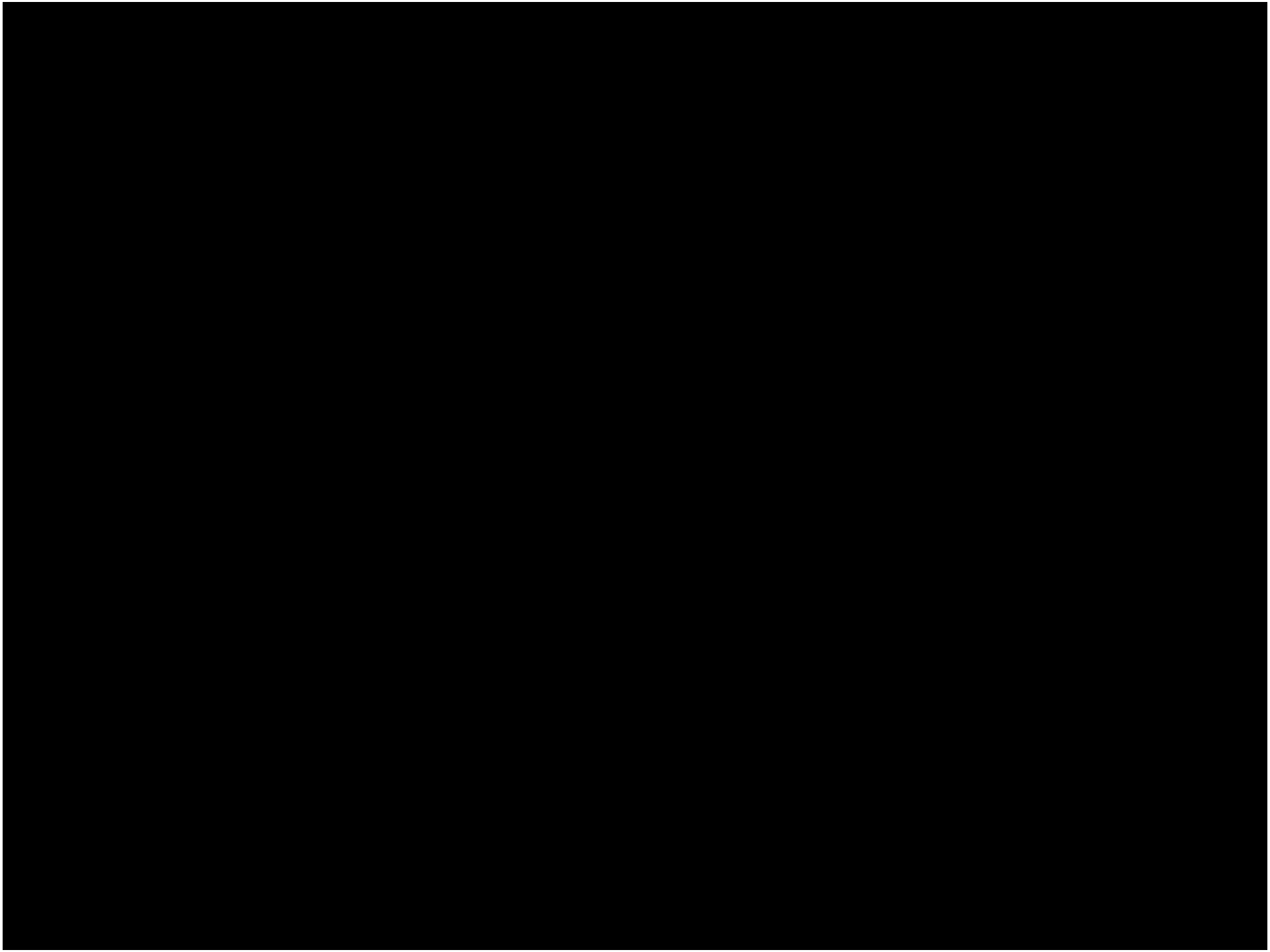
Augusto Fagnola	ICI-UNGS	Oscar Piro	LANADI-UNLP
Martín Blasco	Inquimae	Ricardo Baggio	Tandar-CNEA
Héctor R. Gallo	ICI-UNGS		

$ Conicet - ANPCyT - UBACyT - Antorchas - UNGS - SETCIP-ECOS





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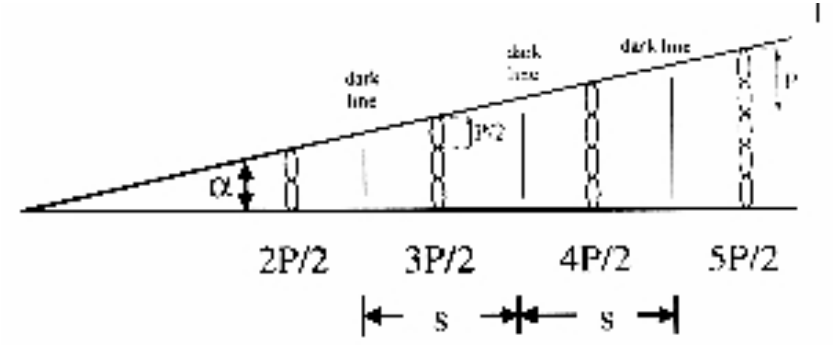

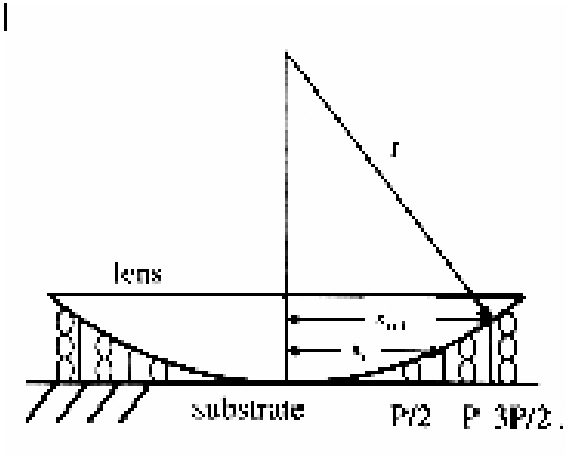

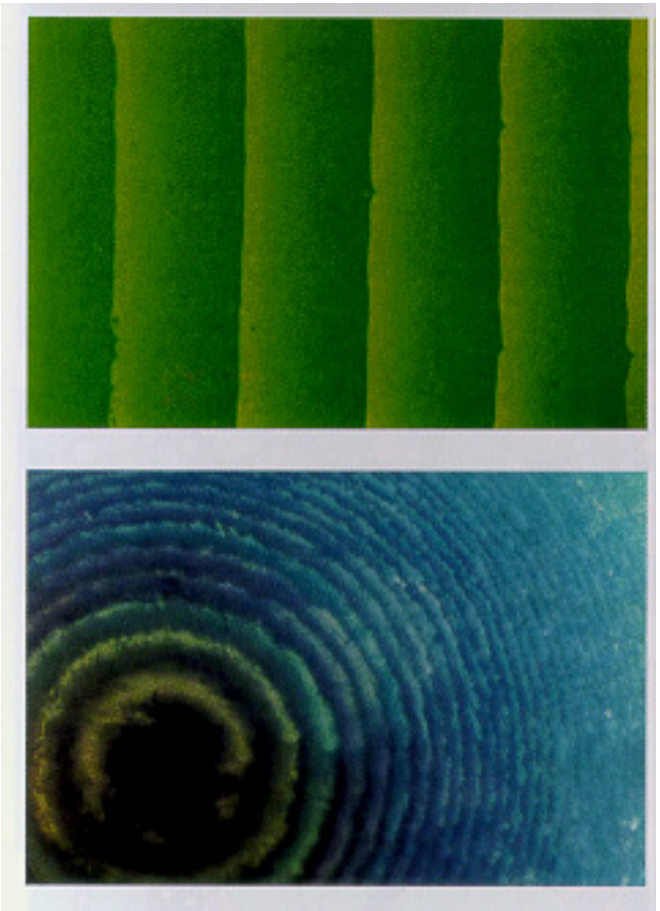

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