

Simulation of Mesogenic Diruthenium Tetracarboxylates: Development of a Force Field for Coordination Polymers of the MMX type

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A classical molecular mechanics force field, able to simulate coordination polymers (CP) based on ruthenium carboxylates ($\text{Ru}_2(\text{O}_2\text{CR}_{\text{eq}})_4\text{L}_{\text{ax}}$) (eq = equatorial group containing aliphatic chains, L_{ax} = axial ligand), has been developed. New parameters extracted from experimental data and quantum calculations on short aliphatic chains model systems were included in the generalized AMBER force field. The proposed parametrization was evaluated using model systems with known structure, containing either short or long aliphatic

chains; experimental results were reproduced satisfactorily. This modified force field, although in a preliminary stage, could then be applied to long chain liquid crystalline compounds. The resulting atomistic simulations allowed assessing the relative influence of the factors determining the CP conformation, determinant for the physical properties of these materials. © 2013 Wiley Periodicals, Inc.

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Introduction

The design of new molecular materials with adequate physical properties that allow them to perform specific functions (functional materials) requires a significant understanding of the characteristics of the molecular fragments, their spatial organization and interconnection. In this context, liquid-crystalline coordination polymers (CP) form a class of materials expected to exhibit the properties of both CP^[1–3] and metal-containing liquid crystals (LC).^[4–6] Despite their potentiality, CP exhibiting spinal columnar mesophases remain scarce.^[7–11] Among them, bimetallic carboxylates $\text{M}_2(\text{O}_2\text{CR}_{\text{eq}})_4\text{L}_{\text{ax}}$ [L_{ax} = axial ligand; R_{eq} = equatorial ligand, Scheme 1a] have been studied thoroughly in the last years^[10–18] with the purpose of obtaining macroscopically orientable, one-dimensional structures.

Systematic experimental studies on these systems established a solid correlation between the nature of the molecular fragments (M_2 , R_{eq} , and L_{ax}) and the mesomorphic properties of these compounds.^[10–13,17] Given the inherent difficulties to obtain direct experimental information at an atomic level in LC phases, the structural aspects of the columnar mesophases of these compounds have been studied by a combination of different techniques such as XRD in LC phase, local probes (RR, IR, SQUID, and EXAFS), volumetric studies, and single-crystal crystallography of nonmesogenic analogues. In this context, several models for the supramolecular organization of these phases have been proposed.^[8,11,15–19]

Derivatives based on ruthenium alkoxy-benzoates (Scheme 1b; X, Y, Z = H or $\text{OC}_n\text{H}_{2n+1}$) are particularly interesting materials as they exhibit columnar mesophases even below room temperature with long range intercolumnar correlation, high thermal stability,^[20] and interactions between spin centers^[21,22]; they are also able to incorporate solvent (lyotropic LC),^[19,23] modifying their structure and fluidity and facilitating their processability. Moreover, they belong to the MMX type of CP, an increasingly active research field due to the high electrical con-

ductivity some of them have shown^[24–27] as well as to the findings that individual polymeric strands can be manipulated.^[28,29]

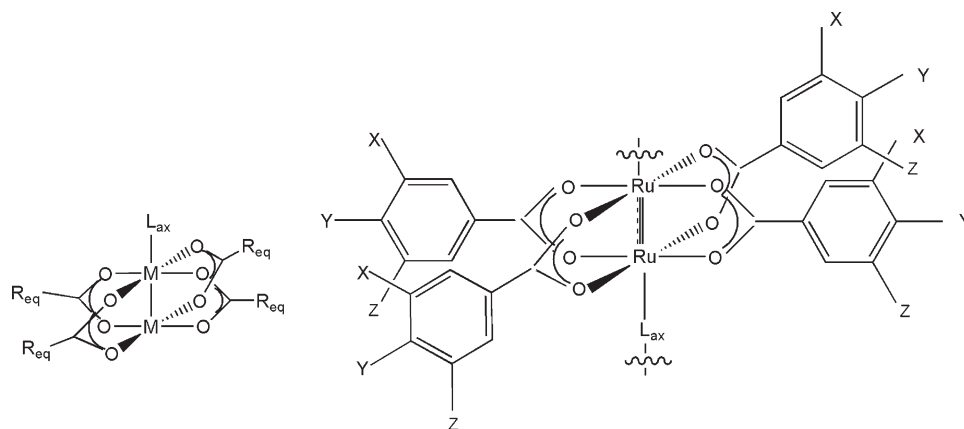
The model proposed^[19] for supramolecular organization in the columnar mesophases of those compounds containing Cl as L_{ax} involves polymeric $\cdots\text{Ru}_2\text{—Cl—Ru}_2\cdots$ strands. Here, the binuclear $\text{Ru}_2(\text{O}_2\text{CR})_4$ units essentially retain the paddle-wheel structure exhibited by all the $\text{Ru}_2(\text{O}_2\text{RCO}_4)_4\text{L}_{\text{ax}}$ compounds, but are tilted one relative to the other, giving rise to zig-zag CP. The structural parameter characterizing the polymer conformation is the Ru—Cl—Ru angle, which seems to result from a compromise between orbital overlap and packing,^[30] and it is modified by the addition of solvents.^[19] The value suggested for the Ru—Cl—Ru angle in this model was consistent with *a posteriori* information obtained from crystallized homologues.^[8]

The conformation of the polymeric backbone plays a crucial role in determining the physical properties of $\text{Ru}_2(\text{O}_2\text{CR})_4\text{Cl}$ compounds, such as their antiferromagnetic interactions and the occurrence of columnar LC phases. As far as the first property is concerned, extensive experimental and theoretical work showed that the extent of the antiferromagnetic coupling strongly depends on the Ru—Cl—Ru angle.^[21,22] As far as the second property is concerned, a preorganization of the CP strands as parallel moieties in the crystalline phase has been shown necessary for the occurrence of columnar mesophases,^[8] as previously suggested for related materials.^[11,31] In order to deepen our understanding on the relative influence

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Scheme 1. Molecular structures of CP based on bimetallic carboxylates and ruthenium alkoxy-benzoate derivatives exhibiting the LC phase analyzed in this work.

of the factors determining the CP conformation, then the physical properties of these materials, we decided to perform an atomistic simulation that allows us to analyze in detail the various factors that affect the organization in the mesophase. The simulations were performed using the AMBER package, which is widely used for the study of conformational problems in biological systems, for which it works very well. Classical force fields, like AMBER's, are usually not parametrized for coordination centers including Ru—Cl, Ru—O or Ru—Ru bonds. Our first task was thus to parametrize the force field for these bonds, as well as the associated angles. Ru—N bonds have also been included in the parametrization step, to provide a force field useful for a wider variety of CP of the $-\text{[MM-L}_{ax}\text{]}-$ type.

The missing parameters were derived using previous quantum mechanical (QM) calculations on these systems,^[30,32] then evaluated against systems with known structure (test cases) where the experimental results were reproduced fairly well. This force field was used to analyze the influence of the equatorial ligand on the conformation of the mesogenic polymers. Octameric strands $[\text{Ru}_2(\text{O}_2\text{CR}_{eq})_4\text{L}_{ax}]_8\text{L}_{ax}$ have been considered for the calculations, which have been performed on two-dimensional arrays to simulate the LC phases.

As we move toward accurate simulations in the mesoscale, atomistic simulations of LC started quite recently to provide answers to structural questions on their mesophases, but remain scarce.^[33,34] Very recently, atomistic calculations have also been used to simulate the LC phase of multi-block mesogens^[35]; our mesogenic Ru compounds can be considered within this category. To the best of our knowledge, this is the first atomistic simulation on LC containing second-row transition metals.

Methods

Quantum mechanical calculations were performed with density functional theory as implemented in the Gaussian 03 and Gaussian 09 packages.^[36,37] We used Becke's three parameter hybrid functional with the correlation functional of Lee, Yang, and Parr formalized as the B3LYP hybrid functional.^[38–41] Unrestricted open-shell calculations were performed in every case. The effective core potential basis set LanL2DZ^[42–45] was used as it pre-

sented the better compromise between accuracy and computational cost. All structures were fully optimized in vacuum and harmonic frequency calculations were performed to establish the nature of the critical points (minimum or transition state). No symmetry constraints were used for the optimization.

All molecular mechanics simulations were performed in vacuum with the AMBER10 package,^[46] specific details are found under each section. Restrained optimizations were performed to obtain the classical potential energy surfaces (PES). Like in umbrella sampling,^[47] the PES were calculated from individual 100 ps simulations with a harmonic bias potential ($k = 120 \text{ kcal mol}^{-1} \text{ rad}^{-2}$). The results were processed using the weight histogram analysis method.^[48]

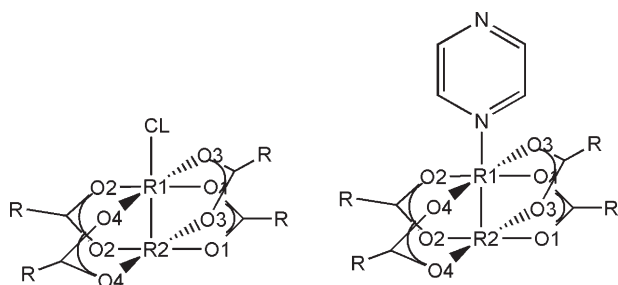
Force field atom types

In order to model the polymers based on ruthenium carboxylates, seven new atom types were included in the generalized AMBER force field (GAFF), Table 1 and Scheme 2a. Depending

Table 1. Atom types not included in GAFF and their respective Lennard-Jones parameters^[49,50].

Atom type	Description	σ (Å)	ϵ (kcal mol ⁻¹)
R1, R2	Ru in O_h environment, Ru—Ru bond	2.34	0.438
O1, O2, O3, O4	O in COO^- equatorial Ru—Ru bridge	0.21	1.6612
CL	Cl bridge	0.265	1.948

on the metal–ligand interaction to be parametrized, an appropriate target compound was chosen: $[\text{Ru}_2(\text{CH}_3\text{COO})_4]_2\text{Cl}_3^-$ and $[\text{Ru}_2(\text{CH}_3\text{COO})_4]_2\text{pz}_3$ (pz = pyrazine, Scheme 2b). So as to define angles and dihedrals unambiguously, it proved necessary to assign a different atom type to each ruthenium atom. In turn, given the octahedral environment around Ru, a different atom type was assigned to each pair of O atoms in a carboxylate bridge in order to have properly defined parameters. As shown in Scheme 2, the angle O—Ru—O is 90° in some cases and 180° in others, and such topologies are not included in the AMBER force field. A new atom type for chlorine acting as a bridge between Ru atoms was included. Lennard-Jones parameters for each atom type are also shown in Table 1.



Scheme 2. Labelling scheme of the new atom types included in AMBER.

Bond length and bond angle terms

Starting parameters were obtained from QM calculations for the model dimers (optimized geometry, normal modes) using the Hessian matrix.^[51] The torsional parameters were initially set to zero. With this methodology, initial parameters were assigned to the Ru—Ru, Ru—O, O—C, Ru—Cl and Ru—N bonds, and to the Ru—Ru—O, O—Ru—O, O—C—C, O—C—O, Ru—O—C, Cl—Ru—O and Cl—Ru—Ru angles. The refined parameters describing the stretching and the bending interactions were determined by fitting the classical potential to the *ab initio* PES of the model compounds, Tables 2 and 3.

With the aim of testing the bond parameters, normal mode calculations were performed with the proposed force field and compared to those obtained both experimentally and through QM calculations, Table 4.

It was observed that the frequencies obtained were consistent with both experimental and QM values with only a slight discrepancy in the case of the Ru—Ru vibration. As bond distances show only small deviations from the equilibrium value and are, therefore, not usually involved in conformational changes, no further refinements were considered necessary.

The questions we would like to address in this work point essentially to the conformation of the polymeric strands in the LC state; this conformation is mainly characterized by Ru—Cl—Ru, N—Ru—O, and C—N—Ru angles, and certainly does not involve the other bonds and angles that define the paddle-wheel structure (e.g., Ru—O distances, O—C—O angles, etc.), which are expected to show very small variations along the simulations. Indeed, crystal structures of more than 20 Ru₂(O₂CR)₄Cl compounds show almost no variability for structural parameters like Ru—Ru distance (2.27–2.29 Å), Ru—O distances (1.96–2.04 Å), or O—Ru—O angles (87–92° or 176–180°), while Ru—Cl—Ru angle varies from 115 to 180° for different compounds.^[22,54] For the three relevant angles defining the conformation of the polymeric strands (Ru—Cl—Ru for Ru₂(O₂CR)₄Cl compounds and N—Ru—O and C—N—Ru for

Table 2. Refined parameters for bond length terms considering the harmonic expression. $E_{\text{bond}}(l) = \frac{1}{2}k(l - l_0)^2$.

Bond	l_0 (Å)	k (kcal mol ⁻¹ Å ⁻²)
Ru _i —Ru _j	2.414	118.21
Ru _i —O _i	2.068	112.58
O _i —C	1.214	648.00
Ru _i —Cl	2.683	37.69
Ru _i —N	2.360	38.80

Assigned atom types: Ru_i = R1, R2; O_i = O1, O2, O3, O4; Cl = CL; C = c; N = nb (included in GAFF).

Table 3. Refined parameters for bond angle terms considering the harmonic expression. $E_{\text{angle}}(\theta) = \frac{1}{2}k'(\theta - \theta_0)^2$.

Angle	θ_0 (°)	k' (kcal mol ⁻¹ rad ⁻²)
Ru _i —Ru _j —O _i	90.0	6.27
O1—Ru _i —O3	90.0	1.68
O1—Ru _i —O4		
O2—Ru _i —O3		
O2—Ru _i —O4		
O1—Ru _i —O2	180.0	1.62
O3—Ru _i —O4		
Ru _i —O _i —C	120.0	18.07
Cl—Ru _i —O _i	91.26	5.24
Cl—Ru _i —Ru _j	177.13	30.00
O _i —C—O _i	120.0	79.10
O _i —C—C	120.0	70.00
N—Ru _i —Ru _j	172.5	30.00
Ru _i —Cl—Ru _j	170.0	6.57
N—Ru _i —O _i	90.0	20.0
C—N—Ru _i	120.0	15.0
N—N—Ru _i	120.0	15.0

Assigned atom types: Ru_i = R1, R2; O_i = O1, O2, O3, O4; Cl = CL; C = c; N = nb (included in GAFF).

Ru₂(O₂CR)₄pz compounds), the comparison between the QM PES and the classical ones, obtained through restrained optimizations, are shown in Figure 1.

Torsional parameters

Although we initially set the torsional parameters to zero, in order to improve the performance of the force field, nonzero parameters should be assigned to relevant dihedral angles. As the paddle-wheel structure itself is not involved in the conformational changes, the O—Ru—Ru—O, O—Ru—C—O, and Ru—Ru—O—C torsions were not exhaustively refined and were roughly assigned the lowest barrier that ensured the prevalence of the structure, 10 kcal mol⁻¹. For the O—C—C—H and O—C—C—C torsions, the generalized parameters included in GAFF were used. In the case of the dihedrals that include the Cl atom, collinear with the Ru—Ru bond, the only relevant torsion is O—Ru—Cl—Ru. Finally, for the pyrazine bridged polymer, as the angle N—Ru—Ru is almost 180°, only the C—N—Ru—O torsion was considered. In order to obtain the parameters for O—Ru—Cl—Ru and C—N—Ru—O, the classical PES was fitted to the QM PES (Fig. 2, Table 5).

When considering improper torsions, it was necessary to include some terms to ensure coplanarity like in the case of the O—O—C—C atoms of the carboxylate and in order to preserve the structure of the aromatic rings in the nitrogen axial ligands (C—C—N—Ru and C—N—N—Ru), Table 6.

Table 4. Comparison between experimental^[52,53] and calculated (MM and QM) bond frequencies. No scale factors were used.

Bond	ν_{MM} (cm ⁻¹)	ν_{exp} (cm ⁻¹)	ν_{QM} (cm ⁻¹)
Ru _i —Ru _j	270	350	330–370
Ru _i —O _i	416	400–450	410
Ru _i —Cl	220	180	220
Ru _i —N	190	ND	165

ND, not determined; Assigned atom types: Ru_i = R1, R2; O_i = O1, O2, O3, O4; Cl = CL; C = c; N = nb (included in GAFF).

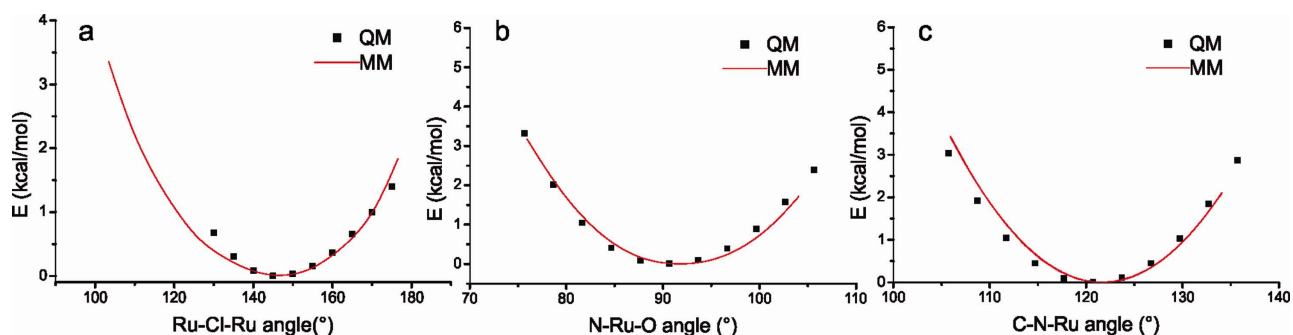


Figure 1. Classical PES for relevant angles, fitted to the *ab initio* PES for (a) Ru—Cl—Ru, (b) N—Ru—O, and (c) C—N—Ru. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Electrostatic interactions

The atomic charges were obtained by fitting the electrostatic potential by both the RESP (restrained electrostatic potential) and the CHELPG (charges from electrostatic potential using a grid based method) method. Both presented equivalent results and the RESP values are shown in Table 7. Compounds under study exhibit point charges higher than those usually found in biological systems, for which AMBER has been parametrized; for this reason, we decided to scale 1–4 interactions with a 0.667 (4/6) factor, instead of the default scaling factor of 0.833 (5/6) included in Amber.^[51]

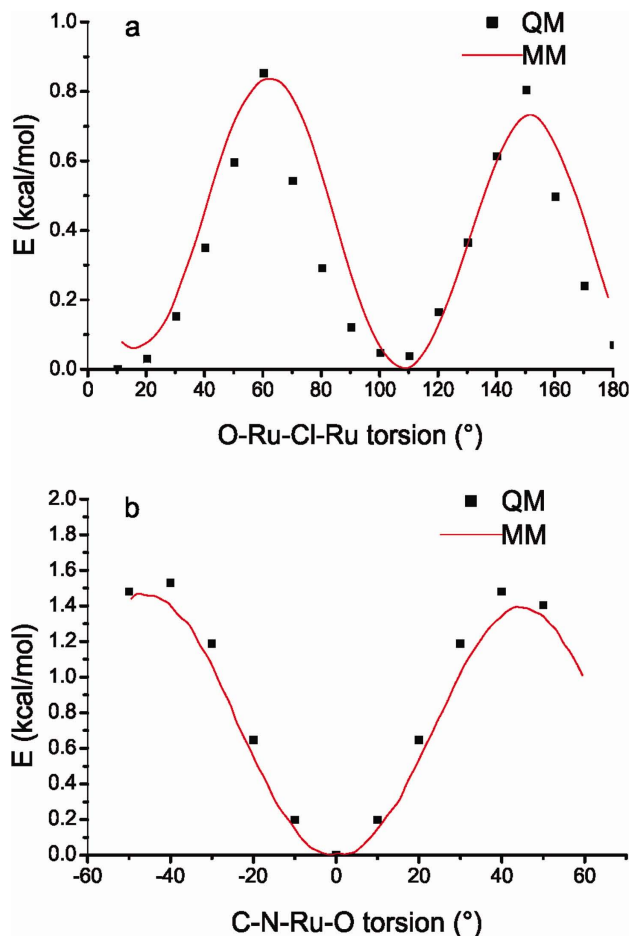


Figure 2. QM and MM potential energy surfaces along the O—Ru—Cl—Ru (a) and C—N—Ru—O (b) torsions. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table 5. Refined parameters for torsions considering the following potential expression $E_{\text{torsion}}(\omega) = \frac{1}{2}v_n(1 + \cos(n\omega - \lambda))$.

Dihedral	$v_n(\text{kcal mol}^{-1})$	$\lambda(^{\circ})$	n
O1—Ru _i —Ru _i —O1	10.0	180.0	2
O2—Ru _i —Ru _i —O2	10.0	180.0	2
O3—Ru _i —Ru _i —O3	10.0	180.0	2
O4—Ru _i —Ru _i —O4	10.0	180.0	2
O1—Ru _i —Ru _i —O2	10.0	180.0	2
O3—Ru _i —Ru _i —O4	10.0	180.0	2
O1—Ru _i —Ru _i —O3	10.0	0.0	2
O1—Ru _i —Ru _i —O4	10.0	0.0	2
O2—Ru _i —Ru _i —O3	10.0	0.0	2
O2—Ru _i —Ru _i —O4	10.0	0.0	2
O3—Ru _i —O1—C	10.0	0.0	2
O4—Ru _i —O1—C	10.0	0.0	2
O3—Ru _i —O2—C	10.0	0.0	2
O4—Ru _i —O2—C	10.0	0.0	2
Ru _i —Ru _i —O _i —C	10.0	180.0	2
O _i —Ru _i —Cl—Ru _i	0.10	240.0	4
C—N—Ru _i —O _i	0.15	180.0	4

Assigned atom types: Ru_i = R1, R2; O_i = O1, O2, O3, O4; Cl = CL; C = c; N = nb (included in GAFF).

Table 6. Refined parameters for improper torsions considering the following potential expression $E_{\text{torsion}}(\omega) = \frac{1}{2}v_n(1 + \cos(n\omega - \lambda))$.

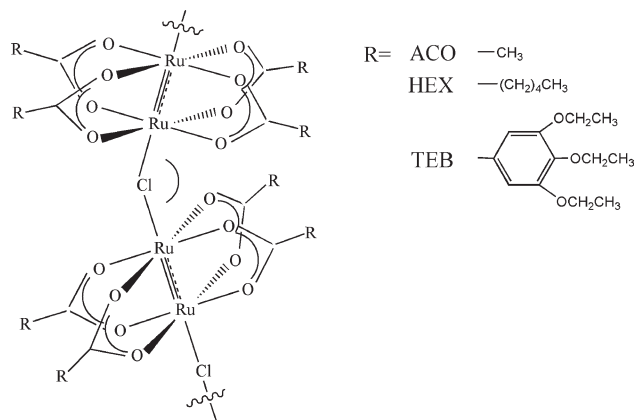
Improper	$v_n(\text{kcal mol}^{-1})$	$\lambda(^{\circ})$	n
O _i —O _i —C—C	10.5	180.0	2
C—C—N—Ru _i	10.5	180.0	2
C—N—N—Ru _i	10.5	180.0	2

Assigned atom types: Ru_i = R1, R2; O_i = O1, O2, O3, O4; Cl = CL; C = c; N = nb (included in GAFF).

Table 7. Atomic charges calculated through RESP method.

Atom	q_{RESP}
Ru _i (Ru ₂ (II,III))	1.2892
Ru _i (Ru ₂ (II,II))	0.8918
O _i	−0.6745
C (COO [−])	0.8399
Cl	−0.5426
N	−0.0460

Assigned atom types: Ru_i = R1, R2; O_i = O1, O2, O3, O4; Cl = CL; C = c; N = nb (included in GAFF).



Scheme 3. Compounds used as tests cases and the relevant geometric parameter Ru—Cl—Ru angle.

Test cases

In order to evaluate the parameters proposed for ruthenium carboxylates, MM calculations were performed for the systems detailed in Scheme 3 with Cl as axial ligand and $\text{Ru}_2(\text{II,III})$. The results were compared with available experimental data.

A single chain of eight monomers (octamer), capped at both ends with Cl^- ions, was simulated in vacuum for each case and the angle Ru—Cl—Ru was analyzed during the simulation as this parameter is highly coupled to the overall conformation of the polymer. Optimizations were performed for the three selected systems ($\text{Ru}_2(\text{ACO})_4\text{Cl}$, $\text{Ru}_2(\text{HEX})_4\text{Cl}$, and $\text{Ru}_2(\text{TEB})_4\text{Cl}$) followed by a 20 ps thermalization at 300 K and 5 ns molecular dynamics at 300 K. In every case, the structure presented a zig-zag conformation consistent with the experimental observations and the QM results in model systems.^[30] When analyzing the Ru—Cl—Ru angle (Scheme 3), one would expect that it would be larger when dealing with aromatic derivatives due to the steric hindrance posed by the rigid benzene rings. However, the opposite effect was observed experimentally as the crystal structures report angles between 115° and 180° for $\text{Ru}_2(\text{ACO})_4\text{Cl}$, 142° for the pentanoate (C5) and 117° for $\text{Ru}_2(\text{TEB})_4\text{Cl}$.^[8] The distributions of the Ru—Cl—Ru angle from the dynamics are presented in Figure 3.

It is observed that the width of the distribution found in the case of $\text{Ru}_2(\text{ACO})_4\text{Cl}$ and $\text{Ru}_2(\text{HEX})_4\text{Cl}$ is larger than for $\text{Ru}_2(\text{TEB})_4\text{Cl}$. For $\text{Ru}_2(\text{ACO})_4\text{Cl}$, the system used for the parameterization, an average angle of 145° is obtained which is consistent with previous QM calculations for a dimer and trimer.^[30] In the case of $\text{Ru}_2(\text{HEX})_4\text{Cl}$, an average angle of 143° is observed, consistent with the experimental data for the ruthenium pentanoate, the closest counterpart. Also in accordance to experimental information, a significant decrease in the average value (120°) is observed for the TEB system. For the latter, some aromatic rings belonging to neighbor binuclear units (monomers) lie in almost parallel planes, 3.3 to 4.0 Å apart (Supporting Information Fig. S1), a typical distance for coplanar aromatic rings undergoing nonbonding (π -stacking) interactions. One of the O—C—C—C dihedrals takes a value between 5 and 10° which agrees with the experimentally observed ones of 0, 3, and 13° .^[8] A comparison of this geometry with the ones predicted for nonaromatic carboxylates, as well as the smaller dispersion found in this case for the Ru—Cl—Ru angle, suggest that nonbonding interactions between the aromatic rings could be responsible for the low Ru—Cl—Ru angle observed.

In a second set of simulations, a tetragonal arrangement of octamers (Fig. 4a, $a = b \neq c$, $\alpha = \beta = \gamma = 90^\circ$) for the aromatic derivative $\text{Ru}_2(\text{TEB})_4\text{Cl}$ was simulated in vacuum and the results were compared to the experimentally determined crystal structure.^[8] A geometry optimization was performed followed by a 100 ps thermalization at 300 K and 14 ns molecular dynamics at 300 K. The results obtained for the central chain are discussed as they better represent the real environment.

As can be observed from Figure 4b, the carboxylate planes of adjacent monomers in the same oligomer are staggered, in accordance to the crystal structure. On the other hand, the analysis of the Ru—Cl—Ru angle along the simulation, Figure 5, reveals that it fluctuates around a larger value than the one observed for a single chain. After 4 ns, this value decreases by 10° to reach an average final value of 136° . In the present case, the closest approach of phenyl rings is still between neighbor monomers of the same oligomer (intra-strand): they lie in parallel planes 3.4–4.9 Å apart, a just slightly higher value than the one predicted for a single strand. However, a second type of phenyl–phenyl interaction, involving equatorial ligands belonging to adjacent oligomers (inter-strand), has been identified in these simulations, exhibiting distances in the range 4.4–5.8 Å. Both types of interactions have been found crystallographically (at 4.17 and 5.59 Å, respectively). The additional interactions that can occur in this tetragonal arrangement (dipolar and van der Waals interactions between ethoxy groups of neighboring CP strands, π – π inter-strand) may partially compensate the interactions between aromatic rings found for a single chain, therefore relaxing the Ru—Cl—Ru angle.

Applications

After confirming this extended force field reproduces fairly well the main structural aspects of the “test” compounds, even in its present stage of development, we used it in order to study a system that presents a LC phase. The LC phase is more disordered than the crystalline phase, which makes it difficult to experimentally obtain a detailed description of the

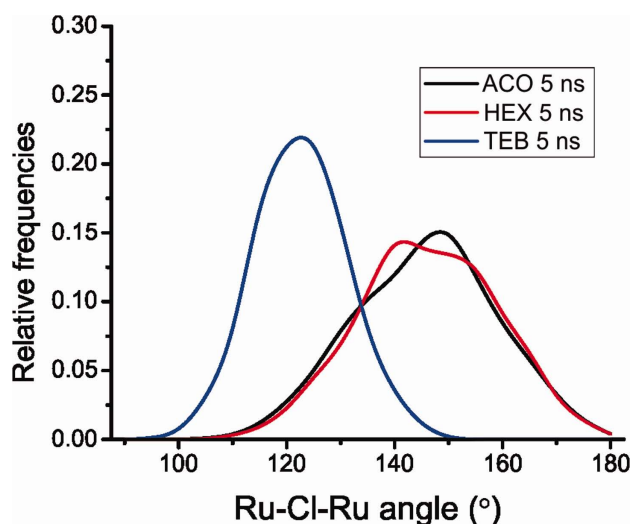


Figure 3. Relative frequencies histogram for the octamers central Ru—Cl—Ru angle for the ACO, HEX, and TEB systems. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

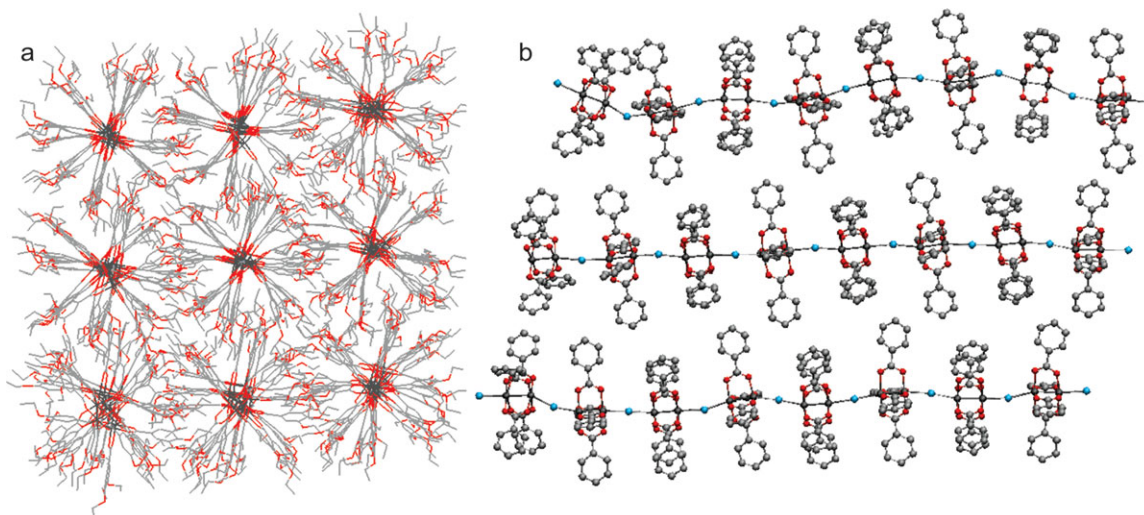


Figure 4. Upper (a) and lateral (b) view of the tetragonal arrangement for $\text{Ru}_2(\text{TEB})_4\text{Cl}$ where the alternated carboxylate planes and the parallel configuration of the close benzene rings can be observed.

structure. For this reason, structural models for LC phases at a molecular level frequently arise from the information obtained through several sources: XRD in LC phase, local probes, volu-

metric studies, and through comparison with crystalline analogues.^[8,18,55–58] In this context, the information provided by the present calculations may allow a deeper understanding of the factors that determine the conformation of the Ru_2 -based CP in the LC phase.

The compound $\text{Ru}_2(3,4,5\text{-}(\text{C}_8\text{H}_{17}\text{O})_3\text{C}_6\text{H}_2\text{CO}_2)_4\text{Cl}$ ($\text{Ru}_2(\text{TOB})_4\text{Cl}$, scheme 4) presents a columnar LC phase from -90 to 294°C with a columnar surface of approximately 504 \AA^2 . The structural model for the LC phase of this compound, proposed on the basis of combined studies like the ones listed in the preceding paragraph,^[8,19] suggests that each column consists of a single polymeric chain where the cores are surrounded by molten aliphatic chains. The estimated distance between Ru_2 centers is 6.3 \AA , which is less than expected if the polymer was in an extended conformation. Therefore, a zig-zag conformation was suggested^[8] which is consistent with our calculations in model systems.

To study this system, a hexagonal arrangement ($a = b = 22 \text{ \AA}$) of seven $[\text{Ru}_2(\text{TOB})_4\text{Cl}]_8\text{Cl}$ strands was simulated in vacuum. A geometry optimization was performed followed by a 100 ps thermalization at 300 K and 10 ns molecular dynamics at 300 K. The results obtained for the central chain are discussed as they better represent the real environment. When analyzing the $\text{Ru}-\text{Cl}-\text{Ru}$ angle along the simulation, Figure 6, it is observed that it decreases until an average value of 141° . Like in the case of $\text{Ru}_2(\text{TEB})_4\text{Cl}$, the carboxylate planes are staggered (Supporting Information Fig. S2) and some aromatic rings belonging to neighbor monomers in the central

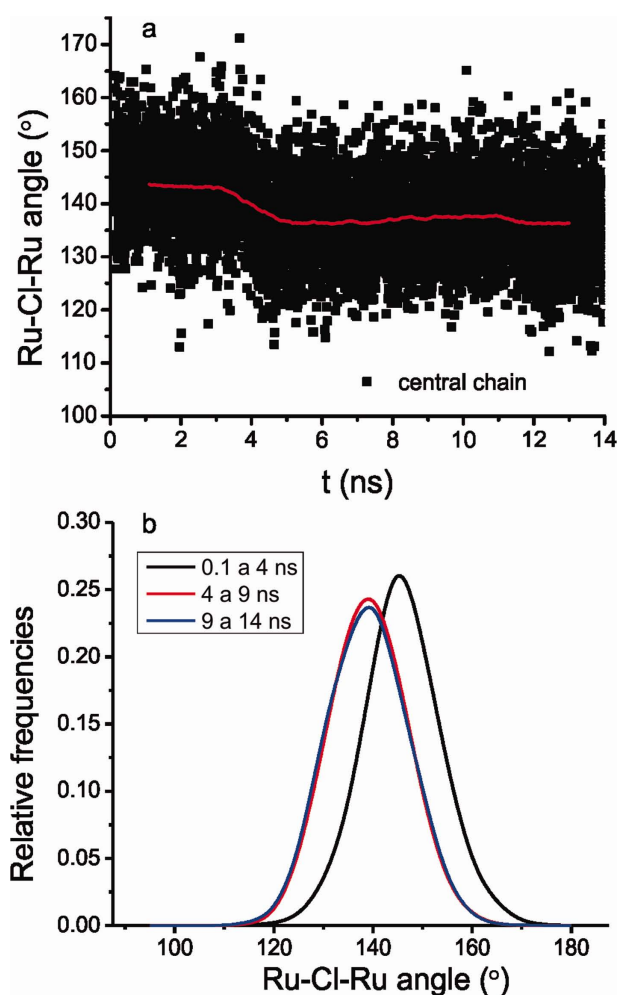
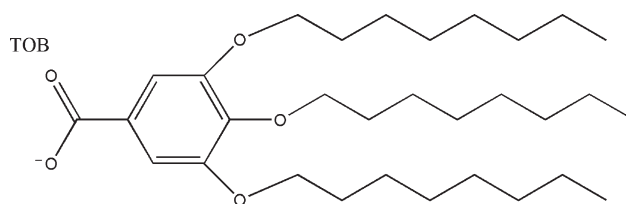


Figure 5. (a) $\text{Ru}-\text{Cl}-\text{Ru}$ angle along the simulation and (b) relative frequencies histogram for $\text{Ru}_2(\text{TEB})_4\text{Cl}$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



Scheme 4. Equatorial ligand of the simulated LC compound.

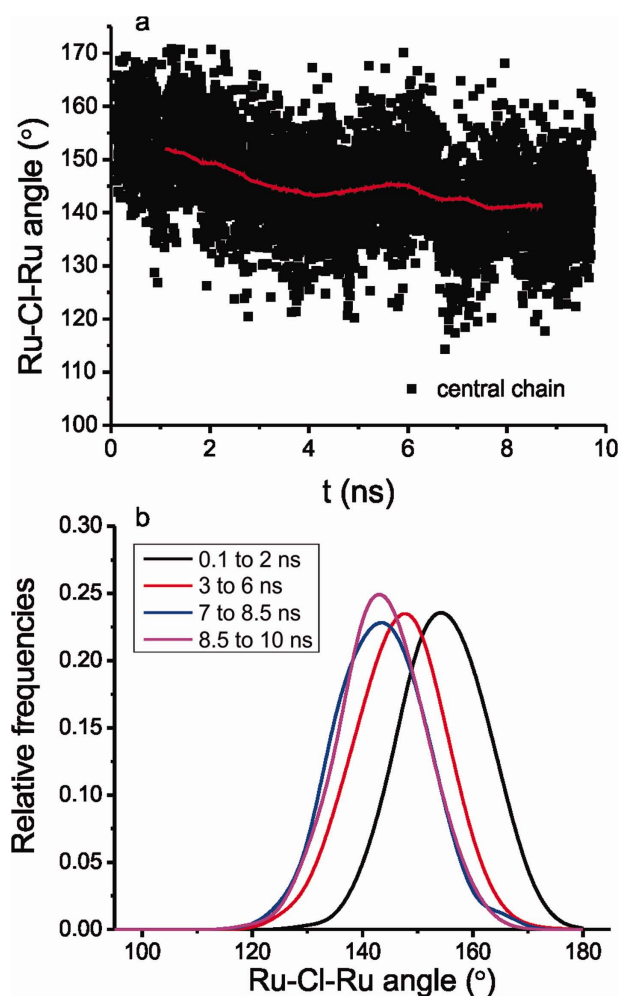


Figure 6. a) Ru—Cl—Ru angle along the simulation and b) relative frequencies histogram for Ru₂(TOB)₄Cl.

oligomeric strand lie in almost parallel planes, 3.8–4.9 Å apart. This value is slightly higher than the one found in the case of the short chain TEB homolog, suggesting, at a first level of interpretation, that in the present case the higher number of methylene–methylene interactions further destabilize π – π interactions. No inter-strand phenyl–phenyl contacts have been detected.

Conclusions

In this work, we described a first parametrization of a classical molecular mechanics force field in order to simulate CP based on ruthenium carboxylates. These parameters were extracted from experimental data and quantum calculations from model systems.

The proposed parametrization was evaluated using model systems with known structure and experimental results were reproduced satisfactorily.

We studied the conformation of selected oligomers in the LC phase, namely some compounds belonging to the Ru₂(3,4,5-(C_nH_{2n+1}O)₃C₆H₂CO₂)₄Cl series. Simulations confirmed the disorder of the aliphatic chains around the central core as

suggested by the model previously proposed,^[8,19] on experimental basis. Moreover, the interaction between the aromatic rings appears to be at the origin of the low Ru—Cl—Ru angle found in these systems compared to that observed on aliphatic derivatives. Overall, the results of these simulations provided additional evidence for a picture in which the conformation of the coordination polymeric [Ru₂(O₂CR)₄Cl]_n strands in the LC phase, characterized by the Ru—Cl—Ru angle, results from a delicate balance of π – π , dipole and van der Waals forces. The relevant role of the interactions between methylene groups and the influence of packing was made evident by comparison between single strands and complex arrangements and between short and long chains.

In addition to the answers provided in this work to specific questions related to structural aspects of the LC phases exhibited by these compounds, the developed force field can be easily transferred to other MMX type CP; in such a case, a more detailed refinement of some parameters (torsional angles, etc.) may be needed.

Keywords: force field · ruthenium carboxylates · MMX polymers · atomistic simulations · liquid crystals

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