

Self-Assembling Columnar Organization in Thallium(I) β -Diketonates: From Crystalline Phases to Liquid Crystals

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In recent years a great deal of research has been devoted to "supramolecular self-organized systems". In most cases, the assembling is achieved by intermolecular hydrogen bonding.¹ This phenomenon is also found in the field of liquid crystals, playing a fundamental role in the organization of the mesophase.² On the other hand, some authors have recently described attractive dimeric and polymeric structures containing Tl atoms, in which short metal-metal contacts commonly occur.^{3,4} Several theoretical works have also been devoted to discussing the existence of Tl-Tl interactions.⁵ The coordinative versatility of thallium and the potential formation of Tl-Tl bonds lead us to include this metal in the synthesis of new metal-organic liquid crystals. Recently we reported two half-disk-shaped aromatic β -diketonato Tl(I) complexes showing a monotropic hexagonal discotic mesophase (**1** and **2**, Table 1).⁶ In the present paper we explore the supramolecular organization responsible for the mesogenic behavior of this novel type of metal-containing liquid crystal, in light of the structural studies carried out in the different aggregation states of these complexes. We have studied the crystalline structure in the solid state of the closely related complex [Tl{(O=CPhOMe)₂CH}] (**3**). This compound has the same molecular core as the two mesogenic β -diketonates **1** and **2**, but the lack of peripheral chains made it possible to obtain single crystals. In addition, powder X-ray diffraction patterns of complexes **1** and **2** were also recorded in the solid phase.

The single-crystal X-ray analysis⁷ carried out for complex **3** shows a crystalline structure based on a monomeric crystallographically independent unit Tl{(O=CPhOMe)₂CH}, where the organic ligand coordinates to the metal center through both ketonic oxygen atoms in a slightly asymmetrical chelate fashion, Tl-O(1) 2.455(6) Å and Tl-O(2) 2.501(6) Å (Figure 1a). These Tl-O bond distances are comparable to those observed in the related [Tl(acac)] complex (2.43 and 2.54 Å),⁸ but are signifi-

Table 1

compound	transitions (°C) ^a
1: R ₁ = R ₂ = O- <i>n</i> -C ₁₀ H ₂₁ ; R ₃ = H	K (94) I I(75) D _{hd} (58) K
2: R ₁ = R ₂ = R ₃ = O- <i>n</i> -C ₁₀ H ₂₁	K (75) I I (69) D _{hd} (20) K K (165) I
3: R ₁ = OCH ₃ ; R ₂ = R ₃ = H	

^aK: crystal. I: isotropic liquid. D_{hd}: hexagonal discotic mesophase.

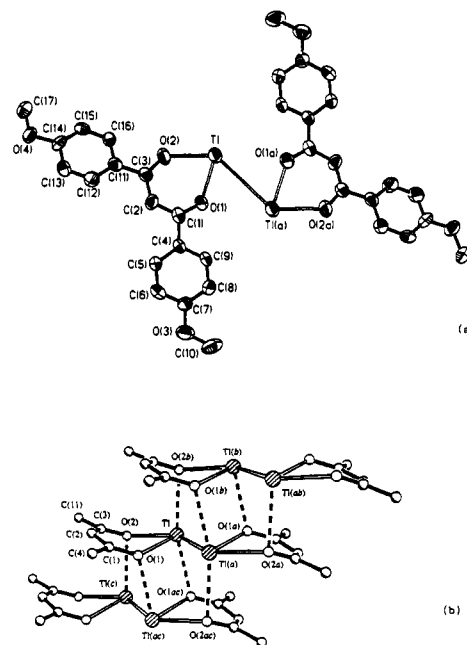


Figure 1. (a) Tl-Tl bonded dimer representation with the labeling scheme used for **3**. (b) Core interactions (Tl-Tl and Tl-O bonds) responsible for the columnar stacking observed.

cantly shorter than the reported values in the hexafluoroacetylacetonate thallium(I) complex [Tl(hfac)], 2.72(3) and 2.62(2) Å.⁹ It is worth noting that both methoxyphenyl substituents are strictly planar and nearly coplanar (dihedral angles 13.2(3)° and -14.6(3)°) with the central coordination plane conferring a planarity to the whole molecule which is useful for the self-assembling of these complexes.

Each monomeric unit is linked to an identical, symmetry-related group through an intermetallic bridged bonding interaction to form a *disk-like* dimer (Figure 1a). The Tl-Tl separation observed is 3.747(1) Å. This distance, only 0.3 Å longer than in Tl metal,¹⁰ is slightly longer than the equilibrium separation obtained by relativistic effective potential SCF calculations for the moiety Tl₂⁰ (3.70 Å) and in the range of typical Tl-Tl contacts in molecular complexes.^{4,5b} The *trans*-bent disposition of the β -diketonate ligand toward the Tl-Tl vector makes a ligand(O(1)-O(2) midpoint)-Tl-Tl(a) angle of 99.8°. This value is within the range described by Hoffmann *et al.*^{5b} for the model compound Tl₂H₂ where the MOs implicated in the Tl-Tl interaction exhibit a positive overlap population, being indicative of a weak bonding nature for this intermetallic interaction. Furthermore, the Tl-Tl distance is significantly

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(7) Crystal data for **3**: C₁₇H₁₅O₄Tl, *M* = 487.67, monoclinic, space group *P2₁/c*, *a* = 4.074(1), *b* = 27.100(3), *c* = 13.756(2) Å, β = 95.14(2)°, *U* = 1512.5(4) Å³, *Z* = 4, *D_c* = 2.142 g cm⁻³.

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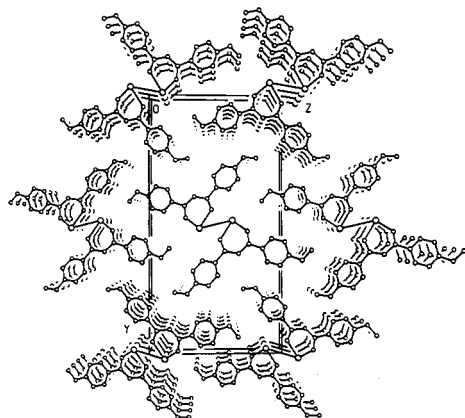


Figure 2. Diagram of the columnar stacking in the structure of **3** viewed along the shortest axis.

Table 2. Lattice Constants and Structural Parameters Determined by Powder X-ray Diffraction^a

compd	phase	structure	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	γ (deg)	<i>Z</i>	<i>U</i> (Å ³)
1	crystal	orthorhombic	30.7	18.4	4.44	90	2	2508
2	crystal	monoclinic ^b	29.45	24.60	8.86	103.0	4	6255
2	mesophase	hexagonal	30.94	30.94		120		

^a Data were taken with a Huber 644 diffractometer using Cu K α radiation ($\lambda = 1.506$ Å). ^b To simplify comparison, a nonstandard setting (*c* unique axis) was chosen for the monoclinic structure.

shorter than that observed in the related complex [Tl₄(OMe)₄], 3.83 Å, where the presence of a weak metal–metal bond has been suggested from the analysis of the vibrational spectra of isostructural complexes, [Tl₄(OR)₄] (R = Et, *n*-Pr).¹¹ If we consider the above facts, it appears that a weak bonding intermetallic interaction is present in **3** contributing to a non-negligible extent to the stabilization of the discotic units. It is noteworthy that the whole dimeric moiety (44 atoms) is roughly planar with a maximum deviation from the mean plane of 0.844(9) Å for the C(13) atom.

Figure 1b shows the stacking disposition of the dimeric units which form a polymeric columnar arrangement along the shortest crystallographic axis. In this peculiar packing the metal is linked to two additional oxygen atoms of the neighboring dimers, one above O(2b) and one below the dimeric moiety O(1ac). These Tl–O distances are longer than those in the plane, but are well below the upper limit described for covalent bonding between oxygen and thallium(I), 3.00 Å.¹² The thallium coordination environment could be described as highly distorted octahedral with a vacant position occupied by the stereochemically-active lone pair of the Tl(I) atom which is located approximately opposite the Tl–O(1) bond. The least-squares planes of two adjacent dimers are separated by 3.2349(4) Å, and the normal of these planes is tilted 34.7(1)° with respect to the crystallographic axis. Figure 2 shows a simplified view of the columnar stacking along the packing direction. This diagram evidences the existence of latent nearly hexagonal columnar stacking.

Powder X-ray diffraction patterns of the two mesogenic complexes **1** and **2** were recorded in the solid state. Table 2 lists the cell parameters for both compounds and the comparative parameters obtained for the mesophase of **2**.⁶ These unit cells (Figure 3a,b) are characterized by the large values of *a* and *b* and the comparatively small value of *c*. It seems reasonable to assume that *a* and *b* must correspond to the lattice dimensions in the plane of the molecules and are consistent with the dimensions of a dimerized complex, whereas *c* must correspond to stacking distances between disks.

In light of the above results we can rationalize the structural

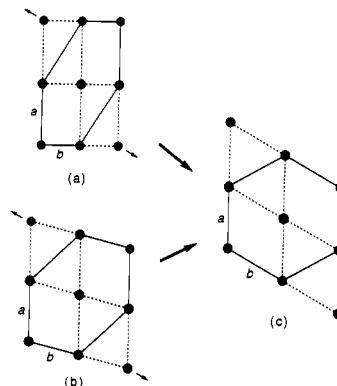


Figure 3. Schematic drawing of the unit cells of complexes **1** (a) and **2** (b) and the mesophase of complex **2** (c) viewed along the *c* axis. The structural distortion can be viewed as a stretching of structures a and b in the direction indicated by the small arrows to give structure c.

relationship between the solid and the liquid-crystalline phases in the following way: The single-crystal X-ray analysis reveals the existence of a columnar stacking of disk-shaped dimers with direct Tl–Tl bonding interactions and axial Tl–O bonds. In the solid state of the mesogenic complexes (**1** and **2**) the order of the paraffinic chains is high enough to keep the columns interrelated, maintaining the three-dimensional structure, as inferred from the powder X-ray experiments. At the melting point the paraffinic chains “melt” and, simultaneously, the axial coordinations between dimers disappear, leading to the transition from the solid to the isotropic liquid. On supercooling of the liquid below the melting point, the intracolumnar axial interactions reappear first, whereas the terminal paraffinic chains remain disordered. At this temperature the transition from the isotropic phase to the mesophase occurs.¹³ In this structural situation the pseudoliquid state of the chains constitutes an almost circular external limit for the formed columns. This cylindrical symmetry which is generated gives rise to a modification of the structure observed in the solid, leading to a hexagonal structure (Table 2, Figure 3).

Additionally, it can be noted that the thallium–oxygen interactions between neighboring molecules should be basically responsible for the stability of the columnar mesomorphic structure. However, the absence of periodicity along the columnar axis, as detected by X-ray measurements, indicates that this stacking is no longer long range.

In conclusion, the X-ray diffraction studies reveal how simple Tl(I) β -diketonate derivatives can give rise to a sophisticated discotic structure, *via* the formation of disk-like dimers by means of intermetallic Tl–Tl bonding interactions reinforced through the formation of Tl–O bonds between neighboring dimers. This dimeric structure is probably stable in the crystalline phases as well as in the proposed discotic mesophase. It is also noticeable that the three-dimensional crystalline structure has a columnar arrangement in which the two-dimensional arrangement of the columnar mesophase is already present.

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Supplementary Material Available: Full details of the crystal structure analysis (10 pages); listing of observed and calculated structure factors for C₁₇H₁₅TlO₄ (10 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

(13) One of the characteristics that differentiates the mesomorphic phase from the crystal is the conformational disorder of the flexible chains, which makes the columns uncorrelate with respect to each other. The diffuse band at 4.4–4.5 Å in the diffraction pattern of the mesophase, characteristic of the molten aliphatic chains, is consistent with this hypothesis.

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