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From High-Temperature Orientationally Disordered Mixed Crystals to Low-Temperature Complex Formation in the Two-Component System (CH₃)₃CBr + Cl₃CBr

Maria Barrio,† Philippe Negrier,‡ Josep Ll. Tamarit,*‡ and Denise Mondieig‡

†Grup de Caracterització de Materials, Departament de Física i Enginyeria Nuclear, ETSEIB,
Universitat Politècnica de Catalunya, Diagonal, 647 08028 Barcelona, Catalonia, Spain
‡Centre de Physique Moléculaire, Optique et Hertzienne, UMR 5798 au CNRS Université Bordeaux I, 351,
cours de la Libération, 33405 Talence Cedex, France

ABSTRACT: The phase diagram of the two component systems (CH₃)₃CBr + Cl₃CBr has been experimentally determined by means of different enthalpy and elasticity calorimetry techniques from the low temperature ordered phases to the liquid state. Before melting, both components have the same orientationally disordered (OD) face centered cubic (FCC) and rhombohedral (R) phases, and the two phase equilibria [FCC + L] and [R + FCC] are accounted for by means of the existence of an isomorphic relationship between the OD phases of pure compounds. The thermodynamic assessment of such equilibria enables us to get the excess properties of the involved OD phases and to rationalize the existence of a maximum and a minimum in the [R + FCC] equilibrium on the basis of the contribution of the entropic term in the excess Gibbs energy function. At low temperature, two complexes, (CH₃)₃CBr:Cl₃CBr (1:1) and (CH₃)₃CBr:2Cl₃CBr (1:2), appear. The structures of 1:1 and 1:2 complexes have been determined to be monoclinic (P2₁/n, c, Z = 4) and hexagonal (P6₃, Z = 6). Within both “ordered” structures, the Cl₃CBr entities of the asymmetric unit were found to be disordered so that sites have fractional occupancies of 0.75 and 0.25 for Cl and Br atoms, in the same way that it occurs for the low temperature monoclinic (P2₁/c, Z = 32) phase of Cl₃CBr. Finally, the existence of complexes is connected with the special intermolecular interactions appearing between a methyl group and a halogen, as previously inferred by Calvet et al. [T. Calvet et al. J. Chem. Phys. 1999, 110, 4841].

1. INTRODUCTION

Simple tetrahedral methylhalogenomethane (MHM) compounds, (CH₃)₄⁺ (X, Y = F, Cl, Br, I, m = 0, ..., 4), have stimulated a large number of experimental studies as well as have been the object of many theoretical works through molecular dynamics simulations to rationalize the intermolecular interactions and the nature of the orientationally disordered (OD) or plastic phases appearing within the rich polymorphic behavior of such compounds. It should be emphasized that this set of compounds constitutes a remarkable case study because these molecules have very close size and a limited kind of intermolecular interactions. These characteristics make systematic studies and comparisons possible.

One of the most outstanding characteristics of the MHM compounds is their pseudospherical shape due to the tetrahedral molecular geometry and similar size of the halogen or methyl group attached to the carbon center. Such a property is the most general of materials displaying an OD phase. Upon increasing temperature from a positional and orientational long range ordered crystal structure, various phase transitions may occur associated with the reduction of some type of order. In the case of pseudospherical shaped molecules, the orientational order is lost first, giving a phase where molecules are able to reorient on their lattice sites, a phase commonly known as plastic phase, a term which is also used to describe the high temperature phase existing just before the liquid state. In spite of the similarity in size and intermolecular interactions, the polymorphic behavior within the realm of MHM compounds at normal pressure (i.e., in equilibrium with its vapor pressure), as well as at high pressure, is known to be quite different, a fingerprint that small differences of size and intermolecular interactions finely tune the thermodynamic functions accounting for the stability of the phases. The stability of the phases can be revealed not only by means of the study of pure compounds, as a function of temperature and pressure, but also by the determination of the phase diagram between two homologous compounds. With the last procedure, the formation of mixed crystals provides information on the thermodynamic mixing properties, thus on the interactions between their molecular units and, in some cases, on the intrinsic polymorphic behavior of the pure compounds.

The case of MHM compounds, the issue of this article, is relevant in two intrinsically linked respects. On one hand, several
molecular dynamics simulation works have proved that, for \((\text{CH}_3)_n \text{C}_\text{Cl} n = 0, ..., 4\) compounds, there is a neat charge transfer from the methyl group to the chlorine centers, in such a way that the methyl group turns slightly positive whereas the chlorine atom turns negative, this behavior being more marked for polar molecules \((n = 1, 2, 3)\) than for nonpolar ones \((n = 0, 4)\). As a consequence, it is highlighted that the dipole moments of the liquid phases are considerably higher than those calculated for the gas phase due to a strong dipole induction exceeding even by about 30% what was estimated until now. These molecular dynamics calculations make then evident the intricate interaction when methyl groups and chlorine atoms are put together.

The second relevant aspect concerns experimental evidence related to two component phase diagrams sharing molecules in which methyl and halogen entities are involved. Some years ago Calvet et al. reported on several binary phase diagrams composed of chemically homologous molecules, in particular, 2 methyl naphthalene + 2 chloronaphthalene and 2 methyl naphthalene + 2 bromonaphthalene, as exceptional cases in which the formation of mixed crystals goes together with the existence of a solid–liquid two phase equilibrium with a maximum. The authors argued through a careful thermodynamic assessment of phase diagrams that the consequence of such exceptionality is the net attraction between methyl and halogen (Cl or Br) which gives rise to negative values of the excess thermodynamic properties of the mixed crystals. The work nicely adds a statistical study on methyl–methyl, halogen–halogen, and halogen–methyl intermolecular contacts among crystal structures collected in the Cambridge Structural Database. The conclusion of this extended analysis is the evidence of a net attraction between the methyl and halogen \((X)\), which the authors wrote in the form:

\[
(-\text{CH}_3 \cdots X^-) > 1/2\{(-X^- \cdots X^-) + (-\text{CH}_3 \cdots -\text{CH}_3)\}
\]

This means that the crossed ("mixed", according to the author’s words) interaction between methyl and halogen is stronger than the average ("unmixed") of those due to methyl–methyl and halogen–halogen.

It should be noticed that within a mixed crystal the attraction between molecules A and B is generally weaker that the mean of the attraction between A and A molecules in the solid state of compound A and the attraction between B and B in B. This common behavior gives rise to a net repulsion which translates to positive values of the energy of mixing generally associated to the common behavior giving rise to negative values of the excess thermodynamic properties of the mixed crystals up to the normal liquid range. It should be kept in mind that the molecular volume difference between these compounds is no more that 2.5%, so the influence of the size in the mixing properties can be neglected.

The polymorphic behavior of these compounds, both formed by molecules with \(C_{3v}\) symmetry, has been recently reported, and it is outlined in Table 1. As for the polymorphism of Cl\(_2\)Br at normal pressure, the lattice symmetry of the low temperature ordered phase is \(C2/c (Z = 32)\), \(27,38\) i.e., isosstructural with the low temperature phases of the subset of the MHM compounds Cl\(_n\)CB\(_r\) \(n = 3, \ldots, 4\). It should be mentioned that, according to this isosstructural character, in the low temperature phase of compounds in which two different halogen atoms are present \((n = 2, 3)\) the molecules are disordered so that sites have fractional occupancies of 0.75 and 0.25, for Cl\(_3\)Br, and of 0.50, for Cl\(_2\)Br, for each of the Cl and Br atoms, respectively. On heating from the monoclinic low temperature phase Cl\(_2\)Br transforms at 238 K to an OD rhombohedral (R) phase, and at

![Figure 1. Two component phase diagrams sharing methylhalogeno-methane derivatives showing maxima and minima in the [R + FCC] two phase equilibria.](image)

**Table 1. Temperatures and Enthalpy and Entropy Changes Associated with the Phase Transitions of \((\text{CH}_3)_3\text{CBr}\) and Cl\(_n\)Br Used in This Work and Previously Reported**

<table>
<thead>
<tr>
<th>transition</th>
<th>(\Delta H/\text{kJ\text{ mol}^{-1}})</th>
<th>(\Delta S/\text{J\text{ mol}^{-1} K^{-1}})</th>
<th>reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>((\text{CH}_3)_3\text{CBr} \rightarrow \text{R})</td>
<td>209.0 ± 1.0</td>
<td>5.90 ± 0.17</td>
<td>28.23 ± 0.80</td>
</tr>
<tr>
<td>((\text{CH}_3)_3\text{CBr} \rightarrow \text{FCC})</td>
<td>208.0</td>
<td>4.12 ± 0.15</td>
<td>27.95 ± 0.48</td>
</tr>
<tr>
<td>((\text{CH}_3)_3\text{CBr} \rightarrow \text{L})</td>
<td>231.8 ± 1.3</td>
<td>0.97</td>
<td>27.44 ± 0.04</td>
</tr>
<tr>
<td>((\text{Cl}_2\text{Br}) \rightarrow \text{FCC})</td>
<td>233.0</td>
<td>1.05</td>
<td>1.04</td>
</tr>
<tr>
<td>((\text{Cl}_2\text{Br}) \rightarrow \text{L})</td>
<td>255.5</td>
<td>1.966</td>
<td>6.77 ± 0.38</td>
</tr>
<tr>
<td>((\text{Cl}_3\text{Br}) \rightarrow \text{M})</td>
<td>238.1</td>
<td>4.38</td>
<td>19.23</td>
</tr>
<tr>
<td>((\text{Cl}_3\text{Br}) \rightarrow \text{L})</td>
<td>238.19</td>
<td>4.618</td>
<td>19.40</td>
</tr>
<tr>
<td>((\text{Cl}_4\text{Br}) \rightarrow \text{FCC})</td>
<td>260.3</td>
<td>0.52</td>
<td>1.98</td>
</tr>
<tr>
<td>((\text{Cl}_4\text{Br}) \rightarrow \text{L})</td>
<td>259.34</td>
<td>0.527</td>
<td>2.03</td>
</tr>
<tr>
<td>((\text{Cl}_5\text{Br}) \rightarrow \text{FCC})</td>
<td>267.1</td>
<td>2.03</td>
<td>7.61</td>
</tr>
<tr>
<td>((\text{Cl}_5\text{Br}) \rightarrow \text{L})</td>
<td>267.9</td>
<td>2.032</td>
<td>7.59</td>
</tr>
</tbody>
</table>

*O refers to the low temperature orthorhombic (Pmn2\(_1\)) phase of \((\text{CH}_3)_3\text{CBr}, M\) to the low temperature monoclinic (C2/c) phase of Cl\(_3\)Br, and \(R\) and FCC to the orientationally disordered rhombohedral and face centered cubic phases.
260 K an OD FCC phase appears, which is stable up to the melting point at 267 K.

As far as (CH₃)₃CBr is concerned, the long time unknown structure of the low temperature phase has been recently determined as orthorhombic (O) Pmn₂₁, and thus the polymorphism has been perfectly established at normal and high pressures.²⁹,³² On heating from the low temperature ordered phase O, it transforms at 209 K to an OD R phase which, on further heating, changes at 233 K to an OD FCC phase, the phase which melts at 255 K.

The similarity between the lattice parameters of both OD R and FCC phases for (CH₃)₃CBr and Cl₃CBr as well as the close size of both molecules suggest the possibility of continuous formation of R and FCC mixed crystals and, according to the previous reports, on the intermolecular interactions between methyl and halogen, the possibility of the existence of singularities (maxima or minima) in the two phase equilibria of the phase diagram. In addition, the question whether such a recognized special interaction between methyl and halogen propagates along the low temperature region can be scrutinized.

This article is organized as follows. In section 2 we provide the experimental details concerning calorimetric and X-ray diffraction techniques conducted for the determination of the two component phase diagram. In section 3 the experimental results and the assessment of the phase diagram to derive the excess properties are presented. Section 4 is devoted to the discussion of results, and finally, we summarize the main conclusions in section 5.

2. EXPERIMENTAL SECTION

2.1. Materials. The chemicals (CH₃)₃CBr (Fluka, purity better than 98%) and Cl₃CBr (Across, purity higher than 99%) were used as purchased without further purification since the measured melting and transition thermodynamic values agreed well with the ones reported earlier.³² Binary mixtures were prepared at room temperature, i.e., in the liquid state, by mixing the materials in the desired proportions.

2.2. Thermal Analysis. A Perkin-Elmer DSC 7 differential scanning calorimeter equipped with a homemade low temperature adapter was used. Heating and cooling rates of 2 K min⁻¹ were used as purchased without further purification since the structural phase changes of the samples were detected either by thermal analysis or by the analysis of short time acquisition patterns as a function of temperature, while long time acquisition patterns were collected at constant temperature (see section 3.3) in the low temperature domain to characterize the formation of complexes. The aim of this study is 3 fold: (i) to limit, as far as possible, the low temperature miscibility regions for the involved phases; (ii) to establish the existence of R and FCC mixed crystals vs mole fraction; and (iii) to characterize the melting transition (Figure 3) as well as the stability domains, especially around the composition domains where complexes appear.

2.3. Excess Enthalpy of the Liquid Phase. The excess enthalpy in the liquid state was determined at 295 K by means of a commercial Biocalorimetre BCP from Electronique Arion for which a homemade mixing cell device was manufactured. The calorimeter and the procedure have been carefully described elsewhere.⁵⁰

2.4. X-ray Powder Diffraction. X-ray powder diffraction data were recorded by means of a horizontally mounted INEL cylindrical position sensitive detector (CPS 120) using Debye—Scherrer geometry (angular step ca. 0.029° 2θ over a 2θ range from 2 to 115°) and equipped with a lithium nitrogen 600 series Cryostream Cooler from Oxford Cryosystems with a temperature accuracy of 0.1 K and similar for fluctuations. Monochromatic Cu Kα₂ (λ = 1.5406 Å) radiation powered with 1.0 kW (40 kW and 25 mA) was selected. External calibration using the Na₂C₅H₃F₄ cubic phase mixed with Silver Béhenate was performed by means of cubic spline fittings. The peak positions were determined by pseudo Voigt fittings. Crystal structures have been resolved by using the modules Powder Indexing for cell searching, the Powder Refinement for full profile determination after pseudo Voigt fittings,³¹ and the module Powder Solve⁵² of the Material Studio application.

Liquid samples were placed at room temperature into 0.3 mm diameter Lindemann capillaries. During data collection, capillaries were rotated perpendicularly to the X-ray beam direction to minimize possible effects of preferred orientations.

3. RESULTS

3.1. Experimental Phase Diagram. By combining differential scanning calorimetry and X-ray powder diffraction, the transition temperatures as a function of composition can be determined to build up the phase diagram. Figure 2 shows the phase diagram from 180 K up to the liquid state. Below 180 K and until ca. 100 K, no phase transitions for mixed crystals or for pure compounds appeared.

The structural phase changes of the samples were detected either by thermal analysis or by the analysis of short time acquisition X-ray patterns as a function of temperature, while long time acquisition patterns were collected at constant temperature (see section 3.3) in the low temperature domain to characterize the formation of complexes. The aim of this study is 3 fold: (i) to limit, as far as possible, the low temperature miscibility regions for the involved phases; (ii) to establish the existence of R and FCC mixed crystals vs mole fraction; and (iii) to characterize the structure of low temperature complexes obtained by means of long annealing times.

The samples were slowly cooled until ca. 100 K and heated again at 180 K where they were annealed and controlled by in situ X-ray diffraction measurements. After the intensity of the main reflections was determined to be constant as a function of time (no less than ca. 12 h), the samples were heated by steps of no more than 5 K, and patterns were collected to determine the equilibrium phases. Such a procedure enabled us to establish the phase transitions as well as the stability domains, especially around the mole fractions close to those where complexes are formed.

The binary phase diagram thus obtained is shown in Figure 2. The main characteristics of the phase diagram may be described as follows. The existence of OD FCC mixed crystals for the whole concentration range can be inferred from the continuous variation of the melting temperatures and the enthalpy change at the melting transition (Figure 3) as well as the continuous variation of the cubic lattice parameter as a function of the mole fraction (see section 3.2), i.e., all the requirements needed for the
existence of an isomorphism relationship between the FCC phases of pure compounds. As for the OD R mixed crystals, the \([\text{R} + \text{FCC}]\) two phase equilibrium interferes with low temperature two phase equilibria in which ordered phases are involved, casting thus doubts concerning the existence of an isomorphism relationship between the R phases of pure components. Such a query is solved by the continuity as a function of mole fraction of (i) the experimental enthalpy change of the R to FCC (Figure 3b), (ii) the R lattice parameters (see section 3.2), and (iii) the existence of one Gibbs function for the R phase for a complete thermodynamic description of the \([\text{R} + \text{FCC}]\) two phase equilibrium (see section 3.4).

As far as the low temperature region of the binary phase diagram is concerned, it can be seen that two new intermediate phases, i.e., complexes, appear around the molar ratios 1:1 (S1) and 1:2 (S2) ((CH\(_3\))\(_3\)CBr:Cl\(_3\)CBr) giving rise to a set of three phase invariants. More specifically, there are two eutectoid invariants, \([\text{S}_2 + \text{R} + \text{FCC}]\) at 205.0 ± 3.0 K and \([\text{S}_1 + \text{O} + \text{R}]\) at 192.0 ± 1.6 K; two peritectoid invariants, \([\text{S}_2 + \text{M} + \text{FCC}]\) at 207.3 ± 1.5 K and \([\text{S}_1 + \text{S}_1 + \text{R}]\) at 198.2 ± 3.0 K; and one metatectoid, \([\text{M} + \text{R} + \text{FCC}]\) at 212.8 ± 1.7 K. Some of the mentioned invariants are clearly visible by means of thermal measurements, but X ray diffraction as a function of temperature was used as previously described to elucidate the intricate sequence of phases. As examples of the used procedure, Figure 4 shows the structural changes when temperature is increased for samples with mole fractions of 0.54 and 0.75.

The enthalpy changes associated with the melting of the OD FCC mixed crystals as well as with the R to FCC phase transition, derived from the DSC measurements, are depicted in Figure 3b. As for the OD R mixed crystals, a similar procedure was used. Lindemann capillaries were slowly cooled to 215.2 K. At this temperature, OD R mixed crystals are stable from \(X = 0\) to about 0.45, whereas for mole fractions higher than about 0.80 they were found to be persistent enough for the lattice parameters to be determined. Figure 5b shows the determined lattice parameters as a function of the mole fraction. Filled circles correspond to supercooled FCC mixed crystals.
3.3. Low-Temperature Complexes. The lattice parameters and space groups of the complexes were obtained from long time acquisition X-ray powder diffraction patterns at 180 K after 12 h annealing, using X Cell software available in the module Powder Indexing of Material Studio package. At this stage the number of molecules in the unit lattice ($Z$) was calculated by assuming a density close to that of pure compounds. The cell parameters and space group compatible with the experimental X-ray diffraction pattern were initially determined using a Pawley profile fitting procedure. By means of Pawley refinement minimizing the weighted R factor ($R_{wp}$, describing the agreement between the experimental pattern and the simulated one), the indexing result was confirmed. The 2θ zero correction and the peak width asymmetry parameters were simultaneously determined. In addition, the analysis of the systematic absences made it possible to determine the possible space groups.

To fully characterize the structure of the low temperature complexes, the molecular structures as rigid bodies previously used for low temperature phases of pure compounds Cl$_2$CBr and (CH$_3$)$_3$CBr were taken. It is noteworthy that for the former molecule it was assumed that the fractional occupations of the halogen sites were set as 0.25 and 0.75 for Br and Cl atoms, respectively, and thus the rigid body entity represents a pseudo structure with tetrahedral symmetry in which overlapping Br and Cl atoms are located at 1.939 and 1.772 Å from the central carbon atom C.

Working within the constraints of rigid molecules, the $Z$ pseudo molecular entities forming the complexes, (CH$_3$)$_2$CBr and Cl$_3$CBr, and (CH$_3$)$_2$CBr and 2Cl$_2$CBr for the 1:1 and 1:2 complexes, respectively, were placed in the unit lattice with the corresponding rotational and translational degrees of freedom to be refined by means of the Powder Solve program. This means that 12 parameters for the 1:1 complex and 18 for the 1:2 complex, in addition to the four preferred orientation parameters according to the March-Dollase function, were obtained. The fitting procedure by Powder Solve coherently succeeded and confirmed the space groups previously quoted by the systematic extinctions of the initial indexing performed by the Powder Indexing module.

Finally, within the rigid body constraint, the structures of the complexes were submitted to a Rietveld refinement, and all the parameters were left free again. For this last procedure, preferred orientation corrections were fitted according to the Rietveld—Toraya parameters function. The following sections detail the structural characteristics of each complex.

<table>
<thead>
<tr>
<th>Table 2. Results from the Rietveld Refinement of (CH$_3$)$_2$CBr:Cl$_3$CBr and (CH$_3$)$_2$CBr:2Cl$_3$CBr Complexes at 180 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>parameter</td>
</tr>
<tr>
<td>2θ-angular range</td>
</tr>
<tr>
<td>2θ-shift (zero correction)</td>
</tr>
<tr>
<td>Profile Parameters</td>
</tr>
<tr>
<td>Na</td>
</tr>
<tr>
<td>Nb</td>
</tr>
<tr>
<td>space group</td>
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<tr>
<td>$Z(Z')$</td>
</tr>
<tr>
<td>Lattice Parameters</td>
</tr>
<tr>
<td>$a$/Å</td>
</tr>
<tr>
<td>$b$/Å</td>
</tr>
<tr>
<td>$c$/Å</td>
</tr>
<tr>
<td>$\alpha$/°</td>
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<tr>
<td>$\Delta$w</td>
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<tr>
<td>overall isotropic temperature factor, $U$/Å$^2$</td>
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<tr>
<td>Preferred Orientation</td>
</tr>
<tr>
<td>(Rietveld—Toraya Function)</td>
</tr>
<tr>
<td>$a^*$</td>
</tr>
<tr>
<td>$b^*$</td>
</tr>
<tr>
<td>$c^*$</td>
</tr>
<tr>
<td>G1</td>
</tr>
<tr>
<td>G2</td>
</tr>
</tbody>
</table>

3.3.1. (CH$_3$)$_2$CBr:Cl$_3$CBr Complex. The experimentally recorded and final calculated profiles of the (CH$_3$)$_2$CBr:Cl$_3$CBr complex are shown in Figure 6 together with the difference plot between them. The parameters of the monoclinic lattice (space group $P2_1/c$) refined according to the described procedure are collected in Table 2, and the coordinates of the atoms of the asymmetric unit ($Z' = 1$) are gathered in Table 3.

The asymmetric unit structure of the (CH$_3$)$_2$CBr:Cl$_3$CBr complex comprises one pseudomolecular entity ($Z' = 1$) formed by one molecule of each molecular species on a general position (Figure 7). Within this “ordered” structure with $Z = 4$ molecules,
the Cl₃CBr entity of the asymmetric unit was assumed to be disordered so that sites have fractional occupancies of 0.25 and 0.75 for Br and Cl atoms, in the same way that it occurs for the low temperature phase of Cl₃CBr and Cl₂CBr₂ compounds. Attempts to order the Br and Cl atoms of the Cl₃CBr entity by fitting the fractional occupancies of the Br and Cl sites did not succeed, confirming the statistical disorder.

3.3.2. (CH₃)₃CBr:2Cl₃CBr Complex. Figure 8 shows the experimental and calculated profiles together with the difference plot between them for the (CH₃)₃CBr:2Cl₃CBr complex at 180 K. The refined parameters of the hexagonal lattice (space group P6₃) are gathered in Table 2, and the coordinates of the atoms of the asymmetric unit (Z’ = 1) are summarized in Table 4.

For this complex, the asymmetric unit comprises one pseudomolecule formed by one (CH₃)₃CBr molecule and two Cl₃CBr molecules, i.e., Z’ = 1. As for the previous complex, Br and Cl atoms occupy sites with fractional occupancies of 0.25 and 0.75, respectively, making evident also the statistical disordered character of the structure (Figure 9).

Table 3. Fractional Atomic Coordinates of the (CH₃)₃CBr:Cl₃CBr Complex at 180 K

<table>
<thead>
<tr>
<th>molecule</th>
<th>atom</th>
<th>X</th>
<th>Y</th>
<th>Z</th>
<th>occupancy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl₃CBr</td>
<td>C</td>
<td>0.0602(6)</td>
<td>0.8478(4)</td>
<td>0.3444(5)</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>Cl</td>
<td>0.1006(8)</td>
<td>1.0034(4)</td>
<td>0.3927(7)</td>
<td>0.75</td>
</tr>
<tr>
<td></td>
<td>Cl</td>
<td>0.0118(8)</td>
<td>0.7681(4)</td>
<td>0.4473(6)</td>
<td>0.75</td>
</tr>
<tr>
<td></td>
<td>Cl</td>
<td>-0.0913(7)</td>
<td>0.8415(6)</td>
<td>0.1889(5)</td>
<td>0.75</td>
</tr>
<tr>
<td></td>
<td>Cl</td>
<td>0.2195(7)</td>
<td>0.7781(4)</td>
<td>0.3486(7)</td>
<td>0.75</td>
</tr>
<tr>
<td></td>
<td>Br</td>
<td>0.1045(8)</td>
<td>1.0181(4)</td>
<td>0.3972(7)</td>
<td>0.25</td>
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<tr>
<td></td>
<td>Br</td>
<td>0.2346(7)</td>
<td>0.7715(5)</td>
<td>0.3490(7)</td>
<td>0.25</td>
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<tr>
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<td>Br</td>
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<td>0.7606(5)</td>
<td>0.4571(5)</td>
<td>0.25</td>
</tr>
<tr>
<td></td>
<td>Br</td>
<td>-0.1056(7)</td>
<td>0.8409(6)</td>
<td>0.1742(5)</td>
<td>0.25</td>
</tr>
<tr>
<td>(CH₃)₃CBr</td>
<td>C</td>
<td>0.5477(6)</td>
<td>0.9363(8)</td>
<td>0.8056(9)</td>
<td>1</td>
</tr>
<tr>
<td></td>
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Figure 8. Final Rietveld refinement plot of hexagonal (P6₃, Z = 6) phase of (CH₃)₃CBr:2Cl₃CBr complex (at 180 K) showing the experimental (red circles), calculated (black line) diffraction patterns and the difference profile (blue line). Vertical bars indicate the calculated Bragg positions. Inset corresponds to the scale for the data with 2θ> 40°.

3.4. Thermodynamic Assessment of the Phase Diagram. The thermodynamic assessment of the phase equilibria concerning the OD and liquid phases has been carried out to derive the excess properties of such phases as well as to infer the truncated part (metastable) of the [R + FCC] equilibrium.

The Gibbs energy for a mixture of (1 – X) mol of pure component A and X mol of pure component B displaying isomorphism in the α phase, i.e., the mixed crystal A₁ ×Bₓ, is connected with the temperature and composition variables by

\[ G^\circ(T, X) = (1-X)\mu_A^\circ + X\mu_B^\circ + RT\ln(X) + G^{\text{EB}}(T, X) \]  

where \( \mu_A^\circ, \mu_B^\circ \) (i = A, B) represents the molar Gibbs energies of pure components A and B; R is the gas constant; \( \ln(X) = (1-X)\ln(1-X) + X\ln X \); and \( G^{\text{EB}}(T, X) \) is the excess Gibbs energy that accounts for the deviation of the mixture in form α from ideal mixing behavior.

Thus, the two phase equilibrium region between two phases (γ and φ) is determined from the minimum Gibbs energy of the mixed crystal \( A_1 \times B_x \) at each temperature. An easy way to proceed, because of the lack of data on \( \gamma_{\text{EB}}(i = A, B) \) and \( \gamma_{\text{EB}}(T, X) \), is the Equal Gibbs Curve (EGC) method. Within this approach, the difference between the Gibbs energies of phases γ and φ can be written as

\[ \Delta G^T\gamma^{-\phi}(T, X) = G^\gamma(T, X) - G^\phi(T, X) = (1-X)\Delta\mu_A^{\gamma^{-\phi}}(T) + X\Delta\mu_B^{\gamma^{-\phi}}(T) + \Delta G^{\text{EB}}(T, X) \]

where \( \Delta\mu_A^{\gamma^{-\phi}} = \mu_B^{\gamma^{-\phi}} - \mu_A^{\gamma^{-\phi}} \) (i = A, B) and \( \Delta G^{\gamma^{-\phi}}(T, X) = G^\gamma(T, X) - G^\phi(T, X) \) is the excess Gibbs energy difference between γ and φ phases. Assuming that the specific heat does not change noticeably, \( \Delta\mu_A^{\gamma^{-\phi}} \approx \Delta S^{\gamma^{-\phi}}_A(T) \Delta T^{-1} \), where \( \Delta S^{\gamma^{-\phi}}_A \) is the entropy change for the transition from γ to φ at \( T^{-1} \), and the equation \( \Delta G^T\gamma^{-\phi}(T, X) = 0 \) provides a curve in the T – X plane where γ and φ phases have equal values of the Gibbs energies (the EGC curve). From this equation, the EGC temperature can be obtained as

\[ T_{\text{EGC}}(X) = \frac{(1-X)\Delta H^{\gamma^{-\phi}} + X\Delta H^{\gamma^{-\phi}}}{(1-X)\Delta S^{\gamma^{-\phi}} + X\Delta S^{\gamma^{-\phi}}_B} + \frac{\Delta G^{\gamma^{-\phi}}(T_{\text{EGC}}, X)}{(1-X)\Delta S^{\gamma^{-\phi}} + X\Delta S^{\gamma^{-\phi}}_B} \]
where $\Delta H^f_{\alpha\gamma}$ is the enthalpy change at the $\gamma \rightarrow \phi$ transition for component $i$. It should be recalled that the first term of the right part in eq 3 is close to a straight line when enthalpy and entropy changes of the $\gamma \rightarrow \phi$ transition for pure compounds A and B are similar, and thus, the deviation from such a behavior is mainly accounted for by the magnitude of the $\Delta G^{E,\gamma\rightarrow\phi}(T, X)$.

By using the experimental data of the [FCC + L] and [R + FCC] equilibria, the procedure to obtain the excess Gibbs energy difference close to the EGC curve, $\Delta G^{E,\gamma\rightarrow\phi}(T_{\text{EGC}}, X)$, has been performed by means of the LIQFIT software. In this framework, the description of each excess property (Gibbs energy, enthalpy, or entropy) is given by an $n$ parameter function in the form of a Redlich–Kister polynomial

$$G^{E,\gamma}(X) = X(1-X) \sum_{i=0}^{n} G_i (1 - 2X)^i \quad (4)$$

Finally, a temperature dependence of the excess Gibbs function can be obtained by the definition of the excess Gibbs energy written in terms of excess enthalpy ($H^{E,\gamma}$) and excess entropy ($S^{E,\gamma}$)

$$G^{E,\gamma}(T, X) = H^{E,\gamma}(X) - TS^{E,\gamma}(X) \quad (5)$$

where both $H^{E,\gamma}(X)$ and $S^{E,\gamma}(X)$ are assumed to be temperature independent magnitudes within the temperature range studied.

The excess enthalpy of the OD phases can be obtained for R and FCC mixed crystals from their melting enthalpy changes and the data of the excess enthalpy of the liquid state (Figure 3). Thus, the enthalpy of a mixture in a $\gamma$ phase can be written as

$$H^\gamma(X) = (1 - X)H^\gamma_0 + XH^\gamma_1 + H^{E,\gamma}(X) \quad (6)$$

and then, the excess enthalpy of the OD phases can be calculated from

$$H^{E,\gamma}(X) = \Delta H^f_{\text{id}} + XH^\gamma_1 + H^{E,\gamma}(X) - \Delta H^f_{\text{id}} \quad (7)$$

where $\Delta H^f_{\text{id}}(X)$ is the enthalpy melting of an ideal mixture, $H^\gamma_1 = (1 - X)\Delta H^\gamma_0 + X\Delta H^\gamma_1 + X\Delta H^\gamma_0$, and $\Delta H^{E,\gamma}(X)$ is the enthalpy effect of the mixed crystals at the $T^{E,\gamma\rightarrow\phi}$ transition.

Equation 7 is applied for $\phi = L$ and $\gamma = \text{FCC}$ and subsequently to $\phi = \text{OD}$ and $\gamma = \text{R}$. Results for the excess enthalpies are reported in Figure 10, whereas the coefficients according to eq 4 are summarized in Table 5.

### 4. DISCUSSION

The analysis of thermodynamic mixing data corresponding to structurally and chemically similar compounds leads to an understanding of the influence of the different factors on the formation of continuous mixed crystals. In addition, the existence of OD and low temperature ordered phases for the involved compounds may help to rationalize the play of orientational disorder into the intermolecular interactions.

Two competing factors ruling the formation of mixed crystals are known to be distinguished: (i) the size and shape of the molecules and the unit cell dimensions, i.e., the steric or geometric
conditions which define the so called geometric mismatch, and (ii) the role of the crossed intermolecular interactions in the mixed crystal structures.

In general, due to the mismatch factor, the mean of the attraction between molecules of different species AB (crossed) is weaker than the average of those of the same species, AA and BB, in such a way that it translates to a net repulsion, i.e., a positive effect on the heat of mixing or, in terms of a thermodynamic function, a positive excess enthalpy of the OD R mixed crystals (see Figure 10), the last distribution has a more pronounced peak than those of CH$_3$···CH$_3$, Br···Br, and CH$_3$···Br. The authors conclude that the CH$_3$···X (halogen) interaction is stronger than the average of the CH$_3$···CH$_3$ and X···X interactions.

In the present case, a parallel quantitative analysis cannot be performed due to the statistical disorder in the Cl$_3$CBr compound which is also mimicked in both complexes. Such a statistical disorder between Cl and Br atoms makes meaningless the halogen–halogen distances from a “real” description of the shortest contacts. A speaking example of this experimental fact is revealed by the Br···Br intermolecular distance within the low temperature structure of Cl$_3$CBr, for which values of 3.575 and 3.740 Å, shorter than the van der Waals diameter of the Br atom, are found. As for the (CH$_3$)$_2$CBr orthonormic low temperature (full) ordered phase, the shortest intermolecular Br···CH$_3$ distances are 3.599, 3.782, 3.851, and 3.861 Å. In spite of the statistical disorder of the halogen sites in both complexes, and assuming that at present the crystallographic tools are the best to describe the real microscopic ordered space, the same analysis has been performed for both complexes. Within this framework, the shortest intermolecular Br···CH$_3$ distances are 3.601, 3.766, 3.804, and 3.829 Å for the 1:1 monoclinic complex and 3.472, 3.524, 3.898, and 3.948 Å for the 1:2 hexagonal complex. For the former, the first shortest distance is similar to that of the orthonormic phase of (CH$_3$)$_2$CBr, whereas the next three shortest distances are relatively smaller. Worth noting are the values for the 1:2 complex, for which the two first shortest Br···CH$_3$ distances are remarkably smaller than those of the pure compound.

This experimental evidence means that the intermolecular interactions CH$_3$···X(halogen) are stronger within the complex than within the pure compound, giving strong support to the arguments and facts provided by the work of Calvet et al concerning the methyl–halogen particular interaction.

Nevertheless, it should be strengthened that this increase of intermolecular interactions evidenced by the shortening of the distances between first neighbors is limited to a short range and...
does not translate into an increase of the packing coefficient (or density), which is a macroscopic magnitude. At 180 K, the packing coefficient for both pure compounds, Cl(CB) and (CH3)3CB, is 0.684 and 0.644, respectively, whereas for the 1:1 and 1:2 complexes it is 0.650 and 0.658, respectively. As the data reveal, packing coefficients of complexes are below those obtained by a linear combination (0.664 and 0.670, for 1:1 and 1:2 complexes, respectively) of the coefficients of the pure compounds.

Finally, we would like to mention that formation of complexes between organic compounds has been reported when highly fluorinated compounds are mixed with aromatic hydrocarbons due to their availability of specific attractive interactions such as charge transfer and quadrupole–quadrupole interactions.60 63 For most of these cases, it has been demonstrated that the electrostatic origin of the attractive interaction remains in the liquid state through molecular associations which give rise to strong negative excess properties in the liquid state.62,64 66 Nevertheless, it should be strengthened that the formation of complexes does not require the existence of negative excess enthalpy accounting for the intermolecular interactions in the liquid state, as reported in the present case.

5. CONCLUSIONS

The two component phase diagram (CH3)3CB + Cl(CB) has been determined from the low temperature region involving orientationally ordered phases up to the liquid (L) state. Mixed crystals between the orientationally disordered face centered cubic (FCC) phases of both pure compounds are formed for the whole composition range, evidence of the isomorphism relationship between both. As for the orientationally disordered rhombohedral (R) phase, the continuous formation of mixed crystals is truncated by the interference of the low temperature two phase equilibrium involving ordered phases with the [R + FCC] equilibrium. Nevertheless, the thermodynamic assessment of the [FCC + L] and [R + FCC] equilibria enables us to conclude the existence of an isomorphism relationship between both R phases. Of special relevance in this two component system is the maximum and minimum for the [R + FCC] two phase equilibrium because there are very few systems showing a solid–solid equilibrium with such extremes.45 Similar behavior was observed concerning the methyl–halogen particular interaction.44

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