Lead(II) and Bismuth(III) Complexes with Macrocyclic Ligands

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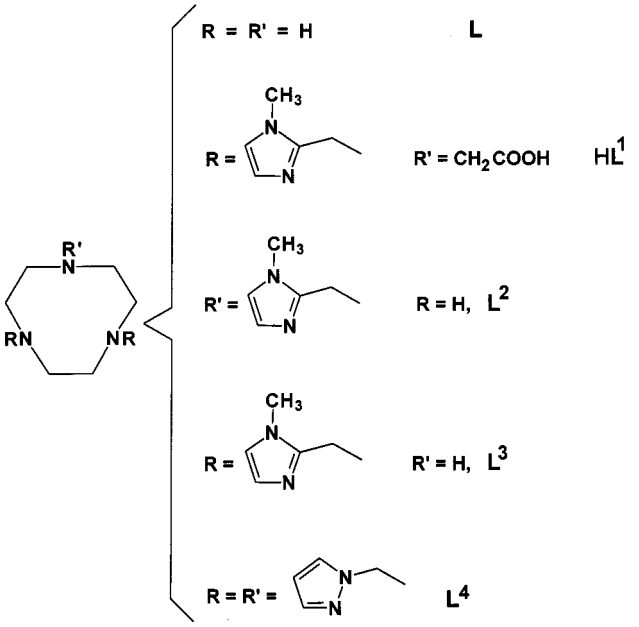
The preparation and X-ray characterization of a Pb^{2+} and a Bi^{3+} complex formed with macrocyclic ligands are reported. In the dimeric complex $[\{Pb(CH_3COO)\mathbf{L}BPh_4\}_2]$, where **L** is 1,4,7-triazacyclononane, the metal atoms are chelated by **L** and bridged by an acetate group; moreover, each of the metal atoms is at contact distance from a tetraphenylborate phenyl group, which completes the coordination. The unsymmetrically derivatized macrocycle 1-carboxymethyl-4,7-bis(1-methylimidazol-2-ylmethyl)-1,4,7-triazacyclononane ((AUTHOR: Substituents are alphabetized: c before m!)), $\mathbf{HL^1}$, in its deprotonated ($\mathbf{L^1}$, anionic) form gives the complex of formula $BiCl\mathbf{L^1}BPh_4$ with Bi^{3+}, which contains $[BiCl\mathbf{L^1}]_2^{2+}$ dimeric cations with eight-coodinated Bi^{3+} and bridging acetate groups within the dimer.

Lead is a persistent and ubiquitous toxic metal, and soil contamination by lead is widespread owing to several industrial activities, mainly battery making and recycling, oil refining, and paint manufacturing.[1] Amongst the techniques for lead-contaminated soil remediation that are being investigated, the removal of the contaminant by chelation is apparently the environmentally most sound.[2]

Within the field of the coordination chemistry of lead(II) we are interested in the synthesis and characterization of its complexes with functionalized macrocycles. In the course of these studies we have found that lead(II) coordinated to 1,4,7-triazacyclononane bearing one, two, or three appended groups ($\mathbf{L^2}$, $\mathbf{L^3}$, $\mathbf{L^4}$) (Scheme 1) further interacts in an η^6-C_6H_5 fashion with a phenyl group of a BPh_4^- anion.[3][4] These results show that the contact interaction of BPh_4^- with lead(II), although unprecedented, is not fortuitous as long as functionalized macrocycles of the above nature are employed. With the aim of further investigating the conditions that make the BPh_4^- interaction with a metal ion feasible, we have prepared a lead(II) complex with the unsubstituted macrocycle 1,4,7-triazacyclononane **L** in the presence of $NaBPh_4$. In the course of investigations into an analogous trend in bismuth(III) complexes we have prepared a Bi^{3+} complex of the unsymmetrically substituted 1,4,7-triazacyclononane $\mathbf{HL^1}$ ligand (Scheme 1). Bismuth(III) is isoelectronic with lead(II) and possesses a similar electronegativity value, but has a smaller ionic radius than lead(II): 103 pm and 119 pm for six-coordinate species.[5] Bismuth and its compounds are regarded as less toxic than lead and have been widely used in traditional medicine.[6] More recently, compounds of bismuth(III) have gained considerable importance because of their potential applications in therapy of cancer[7] (^{212}Bi radioactive isotope) and gastric ulcers,[8] as well as in the technology of high-temperature superconductors.[9] For all these reasons the coordination chemistry of lead(II) and bismuth(III) has attracted increasing attention in recent years, particularly in the search for chelating ligands that may function as efficient metal-sequestring agents (Pb^{2+})[10] and for possible applications in biomedical science (Bi^{3+}).[11–13]



Scheme 1. Ligands referred to in the text

We report here the syntheses and X-ray structural characterizations of the two complexes $[Pb(CH_3COO)\mathbf{L}BPh_4]$ (**1**) (**L** = 1,4,7-triazacyclononane) and $[BiCl\mathbf{L^1}BPh_4]$ (**2**) [$\mathbf{L^1}$ is the deprotonated form of the compound 1-carboxymethyl-4,7-bis(1-methylimidazol-2-ylmethyl)-1,4,7-triazacyclononane, $\mathbf{HL^1}$].

Results and Discussion

The reaction of lead(II) acetate with the cyclic triamine 1,4,7-triazacyclononane **L** and $NaBPh_4$ in MeOH/MeCN solution produces colourless crystals of a compound with the formula $Pb(CH_3COO)\mathbf{L}BPh_4$ (**1**) where a BPh_4^- anion has replaced an acetate anion of the starting $Pb(CH_3COO)_2 \cdot 3\,H_2O$ salt. Two lead(II) complexes formed

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by the **L** macrocycle, Pb**L**$(ClO_4)_2$ and Pb**L**$(NO_3)_2$, have been described previously[14] and their X-ray structural characterizations have shown that, in addition to the **L** macrocycle, both anions are coordinated to lead(II) in each complex, giving rise to highly irregular coordination polyhedra. In order to establish the possible role of the BPh_4^- anion in the coordination of the metal atom in complex **1**, the structure of the compound has been determined. Partly for comparison purposes $BiCl_3$ (Bi^{3+} is isoelectronic with Pb^{2+}) was allowed to react with the macrocycles, shown in Scheme 1, in the presence of $NaBPh_4$. A crystalline product was obtained only when the unsymmetrically functionalized macrocycle 1-carboxymethyl-4,7-bis(1-methylimidazol-2-ylmethyl)-1,4,7-triazacyclononane (**HL^1**) containing an appended acetate group in addition to methylimidazoles, was employed. The complex obtained had the formula Bi**Cl**$\mathbf{L^1}BPh_4$ (**2**) (**L^1** is the anionic form of the **HL^1** ligand) and its crystal structure was determined by X-ray diffraction. The affinity of bismuth(III) for nitrogen donors is considered to be significant and, in particular, larger than that of lead(II).[12][15] In agreement with this, in the formation of **2** most bonds within the $BiCl_3$ reactant are broken and the available coordination sites about the metal centre are occupied by the donor atoms of the macrocyclic ligand, which are predominantly nitrogen atoms. On the other hand, when ligands with uncharged oxygen donors, such as the 4,5,6-donor crown ether, are employed,[13] the $BiCl_3$ unit is found to remain intact and neutral complexes are obtained with non-coordinated oxygen atoms.

The structure of complex **1** consists of $[Pb(CH_3COO)\mathbf{L}BPh_4]_2$ dimers where the monometal fractions, related by a twofold symmetry axis, are joined by an acetate anion in a disordered orientation (Figure 1). Each lead(II) atom is coordinated by the three nitrogen atoms of the macrocycle and by three oxygen atoms from the acetate groups, which have fractional occupancies. In addition, the lead(II) atom is approached at contact distance by a tetraphenylborate phenyl group in a similar fashion to that previously detected for lead(II) complexes formed by the **L** macrocycle bearing various substituents.[3][4] The distance of 3.37(1) Å between the metal atom and the phenyl centroid is within the range (3.06−3.44 Å) of the distances previously found. Each of the acetate anions in the dimer is randomly distributed between two positions related by the symmetry axis. As detailed in the Experimental Section, all fractions of the acetate anions have been assigned a population parameter of 0.5. As a consequence of this, and also given the fact that the position of the bridging (fractional) oxygen atom [O(1)] almost coincides with that of its symmetry-related fraction, the lead(II) atom is surrounded by an oxygen site having full occupancy [O(1) + O(1)′; symmetry operation $1 - x$, y, $1/2 - z$] and by two half-occupied sites [O(2) and O(3)]. The acetate group in the bridging position is also chelating the metal atom through O(1) and O(2), whereas the other group is essentially non-chelating, since its O(4) atom lies at a considerably longer distance from the metal centre than the coordinating O(3) atom (Table 1). In agreement with the arrangement found for the four structures previously investigated, which exhibit a close approach of a phenyl group to the metal atom,[3][4] one macrocycle nitrogen, N(1) in **1**, lies almost *trans* to the phenyl ring while the other two N and the fractional O donors are approximately arranged in a plane almost perpendicular to the N(1)−ring centroid direction. As described previously,[3][4] the metal atom is displaced from that plane in the direction of the phenyl group. The Pb−N distances formed by the unsubstituted triazamacrocycle (mean value 2.50 Å) are shorter than those formed by the macrocycle nitrogen atoms when **L** be-

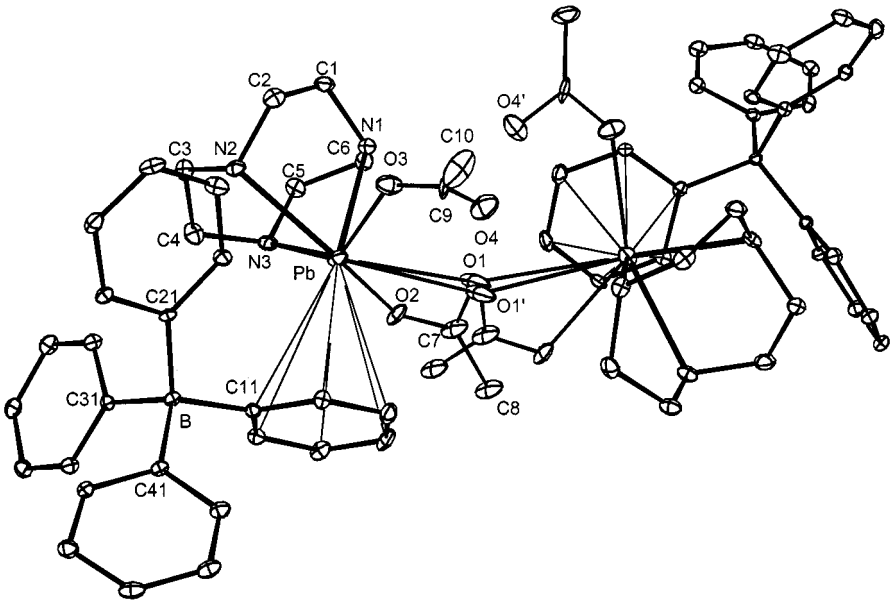

Figure 1. A view of the $[Pb(CH_3COO)\mathbf{L}BPh_4]_2$ dimer in the structure of **1**, showing the atom numbering scheme; all atoms of the acetate groups have a population parameter of 0.5; hydrogen atoms are not shown and only the *ipso*-carbon atoms of phenyl rings are labeled for clarity; primed atoms are related to the corresponding unprimed ones through a twofold symmetry axis

ars substituents (2.52−2.81 Å, range of individual values),[3][4] but are longer than the distances (mean 2.43 Å) found for the two lead(II) complexes formed by the same **L** macrocycle and the coligands with limited space demands ClO_4^- and NO_3^-.[14] The Pb−O distances are in the range of those found for carboxylate complexes.[16]

Table 1. Selected bond lengths [Å] and angles [°] for compound **1**[a−c]

Pb−N(1)	2.423(8)	Pb−O(1)′[b]	2.92(4)
Pb−N(2)	2.558(7)	Pb−O(2)	2.46(1)
Pb−N(3)	2.509(8)	Pb−O(3)	2.60(1)
Pb−O(1)[b]	2.86(4)	Pb···O(4)	3.37(2)
N(1)−Pb−N(2)	70.0(3)	O(2)−Pb−N(1)	86.8(4)
N(1)−Pb−N(3)	70.0(3)	O(2)−Pb−N(2)	137.4(4)
N(2)−Pb−N(3)	68.5(3)	O(2)−Pb−N(3)	70.2(4)
O(1)−Pb−O(2)	38.4(5)	O(3)−Pb−N(1)	79.5(4)
O(1)−Pb−N(1)	76.6(1.3)	O(3)−Pb−N(2)	80.1(4)
O(1)−Pb−N(2)	146.5(1.3)	O(3)−Pb−N(3)	141.8(4)
O(1)−Pb−N(3)	101.3(1.2)	Pb−O(1)−Pb′	149.1(4)

[a] All of the oxygen sites, belonging to the acetate anions, have 0.5 occupancy. Primed atoms are related to the corresponding unprimed ones by a twofold symmetry axis. − [b] The O(1) and O(1)′ sites are almost coincident and together provide one full-occupancy donor atom site in the coordination sphere of each metal atom. − [c] The Pb···C contact distances with the phenyl group carbon atoms are in the range 3.54−3.79 Å.

In agreement with previous results,[3][4] extended Hückel calculations[17][18] on suitable model systems for **1** have shown that the lead(II) lone pair, forming the HOMO of the metal fragment, is neatly oriented away from the region of the "normally" coordinating ligands toward the centre of the phenyl group. This result is practically unaffected by changes to the model aimed at mimicking the partial acetate anion occupancies. Calculations of this type do not account for charge effects and provide rather indirect evidence for the polarization effects that are expected to contribute significantly to the attractive interaction. On the other hand, such calculations stress the repulsive contribution originating from the interaction between the lone pair and the bonding system of the phenyl group. That repulsive contribution is minimized if the lone pair points toward the centre of the phenyl group, as has been shown to occur by the calculations for all five cases investigated. Although the lead(II)/phenyl group interaction under discussion should be considered as a van der Waals interaction augmenting the non-specific ionic component, its surprisingly high strength is revealed by the fact that it appears to be one of the factors that control the packing in the solid state for the compounds in which it has been detected.

Although, in principle, the type of interaction with the tetraphenylborate anion discussed above might be expected to also occur in the bismuth compound **2**, it was found not to be present in that case, probably due to lower extension of the bismuth(III) lone pair compared to that of lead(II) and to the greater importance of ionic interactions in the structure of the bismuth complex. The structure consists of centrosymmetric dimeric $[BiCl\mathbf{L^1}]_2^{2+}$ cations and isolated BPh_4^- anions. Each metal atom is eight-coordinated by the three macrocycle nitrogen atoms and the two methylimidazole nitrogen atoms of the $\mathbf{L^1}$ ligand, by two carboxylate oxygen atoms from different ligands and by the chlorine atom (Figure 2). Each carboxylate group is bridging within the

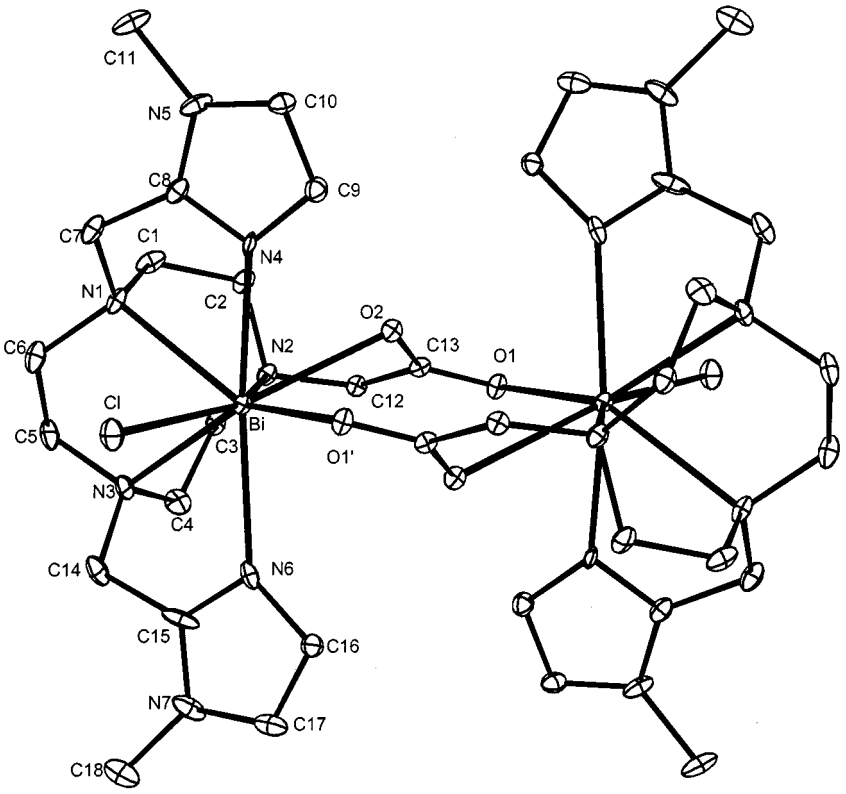

Figure 2. A view of the centrosymmetric $[BiCl\mathbf{L^1}]_2^{2+}$ cation in the structure of **2**; atom O1′ is related to O1 through the inversion centre

dimer, with its two oxygen atoms linked to the different metal atoms. There are five donor atoms [N(1), N(3), N(4), N(6), and O(1)′, symmetry operation $-x, -y, -z$] lying approximately in a plane that also contains the metal atom, with the largest deviations from the plane being < 0.4 Å. The chlorine atom and the midpoint of the two remaining donor atoms N(2) and O(2) define a direction perpendicular to the above plane. Although close comparisons between the present structures are not possible, it is worth noting that the mean value of the distances to the metal centre formed by the macrocycle nitrogen atoms is larger in **2** by 0.22 Å in comparison to **1**, whereas that of the metal−oxygen distances is smaller by 0.14 Å in **2**. These features may again reveal the effect of substituents on the macrocyclic ring, discussed above for the metal−nitrogen interactions in lead(II) compounds, but they may also be due to a higher preference of bismuth(III) for bonds having appreciable ionic character, compared to lead(II). The conformation attained by the $\mathbf{L^1}$ ligand in the bismuth(III) complex differs from the more regular arrangement, approaching threefold symmetry, found for the same ligand in monometal complexes of first-transition-row metal ions.[19] On the other hand, it is not too dissimilar from the arrangement of the pyrazole-trisubstituted macrocycle in the lead(II) complex $Pb\mathbf{L^4}(BPh_4)_2$, where a BPh_4^- phenyl group makes a close approach to the metal atom.[4] By means of extended Hückel calculations on a model of the monometal fraction of the bismuth(III) complex where the environment of the metal atom was schematized in the usual ways,[3][4] with the coordination geometry accurately reproduced, it was verified that the HOMO of the complex essentially consists of the unhybridized metal s orbital, and therefore is without specific directional properties.

Table 2. Selected bond lengths [Å] and angles [°] for compound **2**

Bi−N(1)	2.63(1)	Bi−N(6)	2.54(1)
Bi−N(2)	2.72(1)	Bi−Cl	2.619(4)
Bi−N(3)	2.80(1)	Bi−O(1)′[a]	2.412(8)
Bi−N(4)	2.45(1)	Bi−O(2)	2.601(9)
N(1)−Bi−N(2)	69.0(3)	Cl−Bi−N(1)	81.1(3)
N(1)−Bi−N(3)	65.1(3)	Cl−Bi−N(2)	143.3(2)
N(2)−Bi−N(3)	63.9(3)	Cl−Bi−N(3)	84.7(3)
N(1)−Bi−N(4)	65.5(3)	Cl−Bi−N(4)	88.0(3)
N(3)−Bi−N(6)	62.6(3)	Cl−Bi−N(6)	85.3(3)
N(4)−Bi−N(6)	164.6(3)	Cl−Bi−O(1)′[a]	81.2(2)
O(1)′−Bi−O(2)[a]	75.9(3)	Cl−Bi−O(2)	150.3(2)

[a] The O(1)′ atom is related to O(1) by the inversion centre.

Experimental Section

All reagents were reagent grade. Commercial solvents, when required in the synthetic procedures, were dried according to standard methods and distilled just before use. Hydrated lead(II) acetate (Baker), anhydrous bismuth(III) chloride (Acros), and sodium tetraphenylborate (Baker) were used as received. **L**[20] and $\mathbf{HL^1}$[19] were prepared using procedures reported previously. General experimental methods and measuring techniques were as reported in ref.[19]

$Pb(CH_3COO)LBPh_4$ (1): The salt $Pb(CH_3COO)_2 \cdot 3\,H_2O$ (0.379 g, 1.00 mmol), dissolved in MeOH (20 mL), and a solution of **L** (0.129 g, 1.00 mmol) in MeCN (20 mL) were mixed together at reflux temperature with stirring. Sodium tetraphenylborate (0.684 g, 2.00 mmol) in MeCN (10 mL) was subsequently added to the above mixture and the resulting solution was concentrated nearly to dryness. The residue was redissolved in MeOH and, after addition of EtOH and concentration to a small volume at room temperature, colourless crystals of the complex were obtained. The crystals used for X-ray analysis were obtained by concentration at room temperature of a dilute acetonitrile solution of **1**. − $C_{32}H_{38}BN_3O_2Pb$ (714.65): calcd. C 53.8, H 5.36, N 5.88, found C 53.3, H 5.56, N 5.59. − IR (KBr): $\nu_{asym}(COO^-) = 1590\ cm^{-1}$.

$BiClL^1BPh_4$ (2): $NaBPh_4$ (0.684 g, 2.00 mmol), dissolved in Me_2CO (20 mL), was added with stirring to a boiling solution of anhydrous $BiCl_3$ (0.315 g, 1.00 mmol) and $\mathbf{HL^1}$ (0.376 g, 1.00 mmol) in MeOH (35 mL). On concentrating the resulting solution to a small volume, colourless crystals of **2** were obtained. Recrystallization of the complex from boiling MeCN gave crystals suitable for X-ray diffraction. − $C_{42}H_{48}BBiClN_7O_2$ (938.11): calcd. C 53.8, H 5.16, N 10.5, found C 53.1, H 5.22, N 10.2. − IR (KBr): $\nu_{asym}(COO^-) = 1580\ cm^{-1}$.

Crystal-Structure Analyses: X-ray diffraction data for both compounds were collected at room temperature with an Enraf Nonius CAD4 diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71069 Å). Crystal data and details about structure refinements are given in Table 3. Empirical absorption corrections (ψ scans) were applied. The structures were solved by direct methods[21] and heavy-atom procedures.[22] In the structure of **1**, both acetate anions are distributed over two positions related by the twofold symmetry axis. The two images of the anion in bridging position [atoms O(1)−C(8)] overlap substantially (therefore they cannot exceed the population parameter value 0.5), whereas those of the other anion [O(3)−C(10)] lie apart and may not be mutually exclus-

Table 3. Crystal data, data collection and structure refinement for compounds **1** and **2**

Formula	$C_{32}H_{38}BN_3O_2Pb$ (**1**)	$C_{42}H_{48}BBiClN_7O_2$ (**2**)
M	714.65	938.11
Crystal system	monoclinic	triclinic
Space group	*C*2/*c* (No. 15)	$P\bar{1}$ (No. 2)
a [Å]	33.708(8)	11.454(9)
b [Å]	10.640(2)	13.851(7)
c [Å]	17.748(3)	14.111(5)
α [°]	90	105.31(4)
β [°]	105.70(2)	94.29(5)
γ [°]	90	103.33(5)
V [Å^3]	6128(2)	2079(2)
Z	8	2
$D_{calcd.}$ [g cm^{-3}]	1.549	1.499
Crystal size [mm]	0.20 × 0.35 × 0.50	0.20 × 0.40 × 0.60
μ [mm^{-1}]	5.54	4.35
Collection range [°]	$5 \le 2\theta \le 50$	$5 \le 2\theta \le 50$
Collected refl.	5612	8278
Independent refl.	5377	7287
Obsd. with $I > 2\sigma(I)$	3274	5581
R(int.)	0.037	0.059
No. of parameters	394	489
No. of restraints	18	0
Goodness of fit	1.027	1.096
*R*1 (4)	0.046	0.063
*R*1 (all data)	0.103	0.098
*wR*2	0.134	0.202
Largest res. peak and hole [e/Å]	0.84 and −0.96	2.61 and −1.12

ive, the shortest contact between the two images being O(4)···O(4)′ = 2.55 Å. The possibility that the O(1)−C(8) sites might have an occupancy < 0.5 with the complementary value for the sites O(3)−C(10) could be excluded on the basis of the results (*R* values, thermal parameters values) of test refinements; then, all acetate fractions were assigned the population parameter 0.5. In the final refinement cycles, on F_o^2, all non-hydrogen atoms were refined anisotropically and H atoms were refined using a riding model. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications no. CCDC-106167 (**1**) and -106169 (**2**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: + 44-1223/336-033, E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

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