

Stereoactive lone pair of electrons on bismuth(III): tris(3-hydroxy-2-methyl-4*H*-pyran-4-onato)bismuth(III)

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This manuscript is dedicated to Dr. Arlette Solladié-Cavallo on the occasion of her 70th anniversary

Abstract

Another rare example of stereoactive lone pair of electrons on six-coordinated bismuth(III) – previously unknown tris(3-hydroxy-2-methyl-4*H*-pyran-4-onato)bismuth(III) has been synthesized and characterized by spectral methods (IR, UV, ¹H NMR, ¹³C NMR) and single-crystal X-ray studies. The complex crystallizes in the monoclinic space group $P2_1/n$; $a = 10.495(2)$, $b = 16.240(3)$, $c = 10.788(2)$ Å, $\beta = 91.47(3)^\circ$, $V = 1838.1(6)$ Å³, $Z = 4$, $\lambda = 0.71073$ Å. Conformation of the molecule looks like a butterfly. Atom of the metal has six-coordinated environment and coordination polyhedron as distorted pentagonal pyramid. Molecules of complexes are formed the dimer associates in the crystal packing due to shorten Bi...Bi and Bi...O bonding interactions.

Keywords: Maltol, bismuth(III), NMR spectroscopy, X-ray diffraction, stereoactive lone pair

Introduction

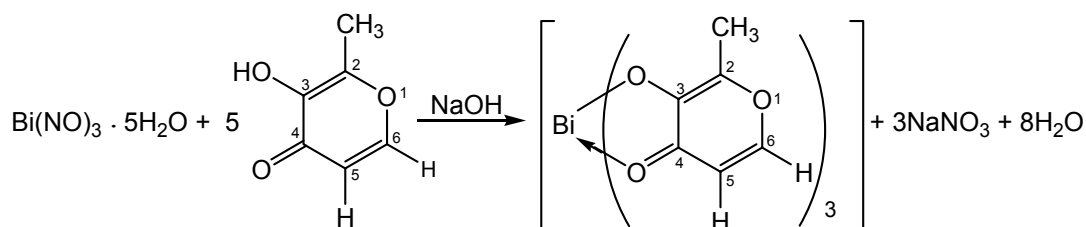
Currently 3-hydroxy-2-methyl-4*H*-pyran-4-one (maltol), an non-toxic (LD₅₀ 1400 mg/kg)¹ chelating ligand of natural²⁻⁵ origin, attracts an ever-increasing interest. This fact is explained by the possible applications of maltol to control the level of metals content in an organism, either by excretion of their excess in the form of metal chelates, through coordination with maltol in the

organism,⁶⁻⁸ or by transportation of necessary metals as chelate complexes to the organism with therapeutic^{9,10} and diagnostic purposes.¹¹⁻¹³

Inorganic compounds of bismuth (trioxide, nitrate) or bismuth acetate are usually used for the treatment of various gastrointestinal diseases as well as the preparation of antiseptic and wound-healing products.^{14, 15} But these drugs possess various side-effects (bismuth stomatitis, dermatitis, nephropathy) related to their toxicity and slow and incomplete excretion from organism.¹⁵ As a result, bismuth complexes prepared on the basis of natural non-toxic maltol, showing antibacterial¹ and antioxidant¹⁶⁻¹⁸ properties may be of special medicinal interest. Thus, the detailed information on structure of maltol-based complexes of bismuth is gaining in importance. This information may also hold a fundamental stereochemical aspect: the stereoactive lone pair on bismuth(III). To the best of our knowledge, only a few compounds of six-coordinated bismuth(III) having a stereochemically active lone pair of electrons (stereoactive lone pair) have been reported,¹⁹⁻²¹ while the overwhelming majority of bismuth compounds have no such lone pair.^{21,22}

Results and Discussion

Tris(3-hydroxy-2-methyl-4*H*-pyran-4-onato)bismuth(III) was prepared by the reaction of maltol with bismuth nitrate pentahydrate. It is known that the ion-coordinative chelation of maltol is favored by its ionization at the O–H bond to form one-charge maltolate-anion $C_6H_5O_3^-$ (L).²³ Therefore, the reaction was carried out in the presence of alkali (2N NaOH), which leads to maltol ionization (pK_a in water 8.6). At the same time the reaction equilibrium was shifted towards the formation of target chelate complex due to the neutralization of acid released during the reaction (Scheme 1).



Scheme 1

According to the elemental analysis data the complex of maltol with bismuth(III) has a stoichiometric ratio metal : ligand of 1 : 3.

In the UV spectrum of the tris(3-hydroxy-2-methyl-4*H*-pyran-4-onato)bismuth(III) (Fig. 1 (b)) in addition to the band at 270 nm (caused partial complex dissociation in the protonodonor solvent resulting to free maltol) appears the band at 312 nm provided $\pi \rightarrow \pi^*$ transition of maltol at anion bonded with Bi^{3+} . That confirmed the position coincidence of observed absorption

maxima at 270 and 312 nm with those of initial maltol (Figure 1a) and maltol in alkaline buffer (Fig. 1 (c)) (where it is present mainly as anion),^{23,24} respectively. Decrease in the excitation energy is caused by the shift of π -electrons across the conjugated chain (polarization) under maltol ionization with formation of the chelate. The bands of charge-transfer (metal-ligand) and $d \rightarrow d^*$ transitions, apparently, have low intensity or these transitions are spin forbidden. Since, they are not registered even at increase of concentration and light way. Besides the position of an observable absorption band at 312 nm does not depend on an electronic configuration of maltol complexes,²⁴ therefore it can not be referred to $d \rightarrow d^*$ transitions or to the charge-transfer band.

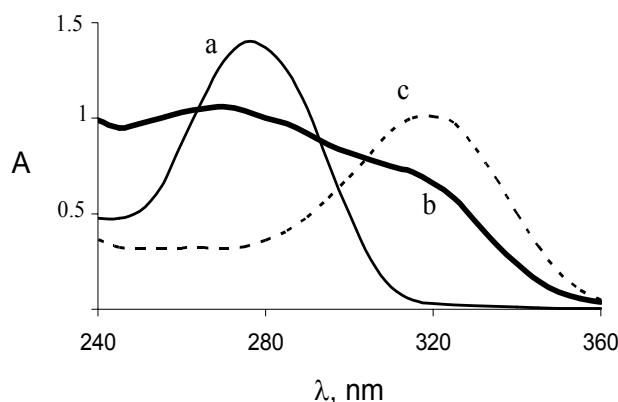


Figure 1. UV spectrum ($c=5 \times 10^{-5}$ M, MeOH): (a) maltol (ϵ_{\max} 28000), (b) tris(3-hydroxy-2-methyl-4*H*-pyran-4-onato)bismuth(III) (ϵ_{\max} 21200, 15000) and (c) maltol (pH=10, $c=6.87 \times 10^{-5}$ M, ϵ_{\max} 14702).

The fact that maltol is bound with metal ion through the oxygen atom of carbonyl group is confirmed by a significant decrease (by 50 cm^{-1}) of valence vibration frequency $\nu(\text{C}=\text{O})$ in IR spectrum of the complex as compared to the spectrum of free ligand (Table 1).²⁵ Disappearance of the absorption band $\nu(\text{O}-\text{H})$ at 3240 cm^{-1} , assigned to maltol hydroxyl, is indicative of the hydroxyl group deprotonation and its coordination with respect to bismuth. The appearance of the bands at 445 cm^{-1} and 251 cm^{-1} proves the availability of the metal-oxygen bond.^{26,27,28} Redistribution of electron density in the chelate results in shift of absorption bands, which correspond to conjugated double bonds of γ -pyrone, toward low-frequency (Table 1).²⁵

Table 1. Characteristic frequencies (ν , cm^{-1}) in IR spectra of maltol and tris(3-hydroxy-2-methyl-4*H*-pyran-4-onato)bismuth(III) in KBr and vaseline oil

Compound	Assignment				
	$\nu\text{O-H}$	$\delta\text{O-H}$ $\nu\text{C=C}$	$\nu\text{C=O}$	$\nu\text{C=C}$	$\nu\text{M-O}$
HL	3240	1660	1625	1565	
BiL ₃			1575	1608	445
				1508	251

¹H NMR spectra of maltol and its bismuth complex (Table 2) provide support for the involvement of OH-group proton in the reaction: the spectrum of its metal derivative show no wide resonant signal at 7.31 ppm, caused by hydroxyl proton. In addition, the resonance signal of H₅, H₆ and CH₃-group protons are shifted with respect their position in maltol that also point to the redistribution of electron density in new metal chelate molecule. So, the signals of H₅ and H₆ protons are shifted towards high field, while signal of the CH₃-group protons – towards low field. Signals of H₅ and H₆ protons of both maltol and its complex are observed as doublets. To assign the carbon signals the ¹³C NMR spectra (without decoupling from protons) and two-dimensional (2D) HMBC ¹H – ¹³C spectra were recorded (Table 2). As is seen from the table the values of coupling constants ¹J_{CH} of C₆ atom are higher than those of C₅ atom that can be explained by neighborhood of the C₆ atom with oxygen atom.

Comparative analysis of ¹³C NMR spectra of maltol and its bismuth complex (Table 2) also proves the formation of chelate compound. So, resonance signals of carbon atoms located near to the coordination center (C₂, C₃, C₄, C₅) are shifted towards lower field. The complex formation seems to be accompanied by the partial deshielding of the ligand carbon atoms that leads to the signals shift observed. The resonance signal of the C₆ atom is shifted (like the signal of the H₆ atom in ¹H NMR spectrum) towards higher field. This effect can be explained by the decrease of conjugation in the γ -pyrone ring.

Crystal structure of the complex is formed by one crystallographic independent molecule C₁₈H₁₅BiO₉ (Fig. 2), taking general position in the unit cell. The conformation of the molecule looks like a butterfly: the heterocycles with O1, O2, O6 and O7 atoms – «wings», are planar. The dihedral angle formed by BiO1C1C2O2 and BiO6C15C16O7 planes is 157.7°. The perpendicular BiO3C8C9O4 plane is the «body of the butterfly». The dihedral angles between this plane and «wings» are 68.9 and 90.7°, for BiO1C1C2O2 and BiO6C15C16O7 planes, respectively.

Table 2. The values of ^1H and ^{13}C NMR (δ , ppm) chemical shifts and coupling constants (J , Hz) of maltol and tris(3-hydroxy-2-methyl-4*H*-pyran-4-onato)bismuth(III)

Compound	^1H NMR					
	H ₅	H ₆	CH ₃	OH		
HL	6.42	7.70	2.36	7.31		
	$^3J_{5,6} = 5.2$	$^3J_{5,6} = 5.2$				
BiL ₃	6.41	7.64	2.42			
	$^3J_{5,6} = 5.1$	$^3J_{5,6} = 5.1$				
^{13}C NMR						
	C ₂	C ₃	C ₄	C ₅	C ₆	CH ₃
HL	149.51	143.44	173.25	113.35	154.22	14.37
	$^2J_{\text{CH}} = 7.4$	$^2J_{\text{CH}} = 2.8$	$^2J_{\text{CH}} = 7.4$	$^1J_{\text{CH}} = 167.9$	$^1J_{\text{CH}} = 199.7$	$^1J_{\text{CH}} = 129.6$
			$^3J_{\text{CH}} = 1.2$	$^2J_{\text{CH}} = 8.5$	$^2J_{\text{CH}} = 6.4$	
BiL ₃	157.42	153.88	179.83	115.22	152.12	15.05
			$^2J_{\text{CH}} = 7.4$	$^1J_{\text{CH}} = 168.0$	$^1J_{\text{CH}} = 196.8$	$^1J_{\text{CH}} = 129.3$
			$^3J_{\text{CH}} = 2.0$	$^2J_{\text{CH}} = 9.0$	$^2J_{\text{CH}} = 6.0$	$^3J_{\text{CH}} = 5.4$

The metal atom is hexa-coordinated in a distorted pentagonal pyramid. The O3 atom is located on the vertex of the pyramid, while O1, O2, O4, O7 and O6 atoms are placed at base of the pyramid. These atoms form distorted pentagon with bismuth atom in the center. Unlike the known octahedral maltolate complexes of six-coordinated Al^{III},²⁹ Fe^{III}³⁰ and thiomaltol complex of six-coordinated Fe^{III},³¹ the formation of distorted pentagonal pyramid of six-coordinated Bi^{III} is determined by the presence of stereoactive lone pair.³²⁻³⁴ This is another rare example of such bismuth compounds.¹⁹⁻²¹

Important bond distances and bond angles for complex appear in Table 4 and 5. The distances Bi–O are unequal – the Bi–O2, Bi–O4 and Bi–O7 bonds are longer (2.481(4), 2.487(3), 2.447(4) Å, respectively) than the Bi–O1, Bi–O3 and Bi–O6 bonds (2.276(3), 2.150(3), 2.275(3) Å, correspondingly) that is indicative of coordination nature of the Bi–O2, Bi–O4 and Bi–O7 bonds and covalence nature of the Bi–O1, Bi–O3 and Bi–O6 bonds. Extension of the Bi–O1 and Bi–O6 bonds in comparison with the Bi–O3 bond is probably related to participation of the O1 and O6 atoms in shorten intermolecular interactions Bi...O1 and Bi...O6 with the distances of 3.140(3) and 3.105(3) Å, respectively (sum of van der Waals radii of the corresponding atoms is 3.9 Å).³⁵ In addition, shorten interaction Bi...Bi having the distance of 3.721(1) Å was found (sum of van der Waals radii is 4.8 Å).³⁵

Table 3. The basic crystallographic data of X-ray diffraction study tris(3-hydroxy-2-methyl-4*H*-pyran-4-onato)bismuth(III)

Parameters	
Formula	C ₁₈ H ₁₅ BiO ₉
Molecular weight	584.28
Syngony	Monoclinic
Space group	P2 ₁ /n
Parameters of elementary cell	
<i>a</i> /Å	10,495(2)
<i>b</i> /Å	16,240(3)
<i>c</i> /Å	10,788(2)
α /°	90
β /°	91,47(3)
γ /°	90
<i>U</i> /Å ³	1838,1(6)
<i>Z</i>	4
λ /Å	0,71073
<i>D</i> _{calc} , /g·cm ⁻³	2,11
μ /mm ⁻¹	9,642
Total number of reflections	3425
Number of independent reflections	3246
Number of reflections with [<i>F</i> ₀ > 4σ(<i>F</i> ₀)]	2269
Number of parameters	254
(2θ) _{max} , °	50,14
<i>R</i> – factor (<i>F</i> ₀ > 4σ(<i>F</i> ₀))	0,029

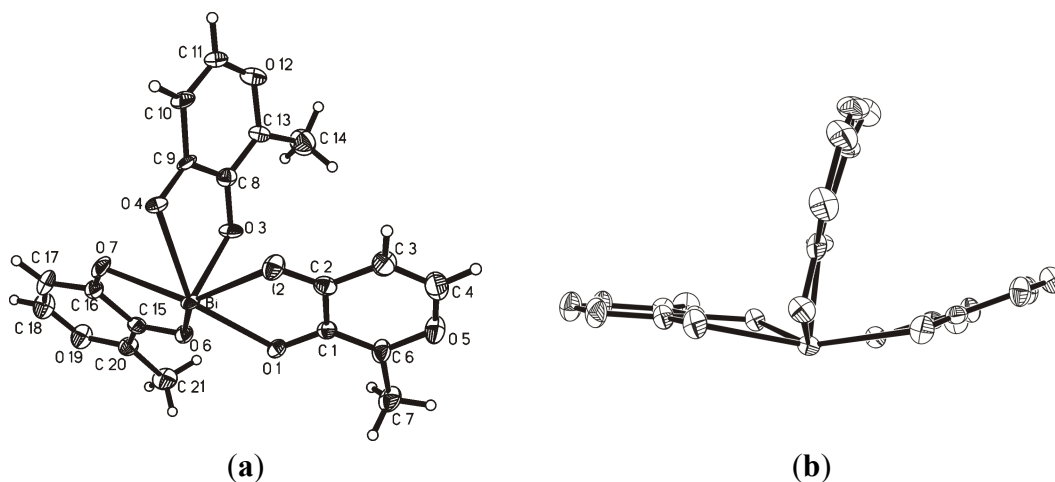
**Figure 2.** (a) molecular structure of tris(3-hydroxy-2-methyl-4*H*-pyran-4-onato)bismuth(III) and (b) conformation.

Table 4. Bond distances (*d*) for tris(3-hydroxy-2-methyl-4*H*-pyran-4-onato)bismuth(III)

Bond	<i>d</i> , Å	Bond	<i>d</i> , Å
Bi-O(1)	2,276(3)	O(19)-C(20)	1,393(7)
Bi-O(2)	2,481(4)	C(1)-C(6)	1,367(7)
Bi-O(3)	2,150(3)	C(1)-C(2)	1,441(7)
Bi-O(4)	2,487(3)	C(2)-C(3)	1,406(8)
Bi-O(6)	2,275(3)	C(3)-C(4)	1,329(9)
Bi-O(7)	2,447(4)	C(6)-C(7)	1,509(8)
O(1)-C(1)	1,321(6)	C(8)-C(13)	1,371(7)
O(2)-C(2)	1,254(6)	C(8)-C(9)	1,452(7)
O(3)-C(8)	1,318(6)	C(9)-C(10)	1,408(7)
O(4)-C(9)	1,250(7)	C(10)-C(11)	1,314(9)
O(5)-C(4)	1,316(8)	C(13)-C(14)	1,486(9)
O(5)-C(6)	1,353(7)	C(15)-C(20)	1,372(7)
O(7)-C(16)	1,239(7)	C(15)-C(16)	1,457(7)
O(6)-C(15)	1,318(6)	C(16)-C(17)	1,422(8)
O(12)-C(11)	1,345(7)	C(17)-C(18)	1,308(9)
O(12)-C(13)	1,360(7)	C(20)-C(21)	1,468(8)
O(19)-C(18)	1,334(7)		

This explains the fact that the bismuth atom, being involved in the additional non-valence interactions, deviates from the base of the pyramid (0.44 Å) in the direction opposite to apical atom O3 towards the metal atom of the neighbor molecule. Due to these contacts dimer associates are formed (Figs. 3, 4), while Bi atom becomes nine-coordinated.

Table 5. Angles (ω) for tris(3-hydroxy-2-methyl-4*H*-pyran-4-onato)bismuth(III)

Angle	ω , °	Angle	ω , °
O(3)-Bi-O(6)	80,9(1)	C(3)-C(2)-C(1)	115,5(5)
O(3)-Bi-O(1)	83,2(1)	C(4)-C(3)-C(2)	121,8(6)
O(6)-Bi-O(1)	73,1(1)	O(5)-C(4)-C(3)	122,2(6)
O(3)-Bi-O(7)	85,1(1)	O(5)-C(6)-C(1)	122,2(5)
O(6)-Bi-O(7)	69,7(1)	O(5)-C(6)-C(7)	112,1(5)
O(1)-Bi-O(7)	142,3(1)	C(1)-C(6)-C(7)	125,6(5)
O(3)-Bi-O(2)	76,0(1)	O(3)-C(8)-C(13)	120,9(5)
O(6)-Bi-O(2)	137,8(1)	O(3)-C(8)-C(9)	120,9(5)
O(1)-Bi-O(2)	69,6(1)	C(13)-C(8)-C(9)	118,1(5)
O(7)-Bi-O(2)	140,7(1)	O(4)-C(9)-C(10)	124,7(5)
O(3)-Bi-O(4)	72,1(1)	O(4)-C(9)-C(8)	119,3(4)
O(6)-Bi-O(4)	133,1(1)	C(10)-C(9)-C(8)	116,0(5)

O(1)-Bi-O(4)	137,4(1)	C(11)-C(10)-C(9)	122,4(6)
O(7)-Bi-O(4)	70,4(1)	C(10)-C(11)-O(12)	121,3(5)
O(2)-Bi-O(4)	71,1(1)	O(12)-C(13)-C(8)	121,4(5)
C(1)-O(1)-Bi	117,4(3)	O(12)-C(13)-C(14)	113,1(5)
C(2)-O(2)-Bi	111,9(3)	C(8)-C(13)-C(14)	125,5(5)
C(8)-O(3)-Bi	117,2(3)	O(6)-C(15)-C(20)	122,0(5)
C(9)-O(4)-Bi	109,4(3)	O(6)-C(15)-C(16)	119,3(4)
C(4)-O(5)-C(6)	119,7(5)	C(20)-C(15)-C(16)	118,7(5)
C(16)-O(7)-Bi	114,1(3)	O(7)-C(16)-C(17)	124,6(5)
C(15)-O(6)-Bi	116,8(3)	O(7)-C(16)-C(15)	119,0(5)
C(11)-O(12)-C(13)	120,4(5)	C(17)-C(16)-C(15)	116,4(5)
C(18)-O(19)-C(20)	119,1(5)	C(18)-C(17)-C(16)	120,7(6)
O(1)-C(1)-C(6)	122,7(5)	C(17)-C(18)-O(19)	124,2(6)
O(1)-C(1)-C(2)	119,1(4)	C(15)-C(20)-O(19)	120,7(5)
C(6)-C(1)-C(2)	118,2(5)	C(15)-C(20)-C(21)	126,3(5)
O(2)-C(2)-C(3)	124,1(5)	O(19)-C(20)-C(21)	113,(5)
O(2)-C(2)-C(1)	120,4(5)		

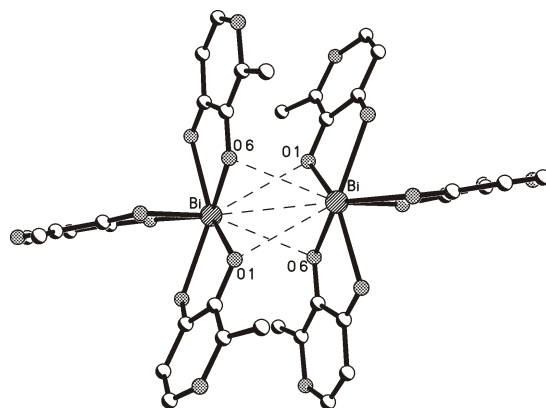


Figure 3. Dimer associate of tris(3-hydroxy-2-methyl-4*H*-pyran-4-onato)bismuth(III).

Particular emphasis is placed upon the extension of the C–O bonds, which are in *cis*-position with respect to methyl substitute: the O1 –C1, O3 –C8 and O6–C15 bond are longer than the O2–C2, O4–C9, O7–C16 bond by 0.07 Å that points to the absence of delocalization of the C–O bonds in metal rings.

Metal rings deviates insignificantly from plane conformation: dihedral angles between BiO1O2/O1C1C2O2, BiO3O4/O3C8C9O4, BiO6O7/O6C15C16O7 planes are 169.2, 171.1 and 170.8°, respectively.

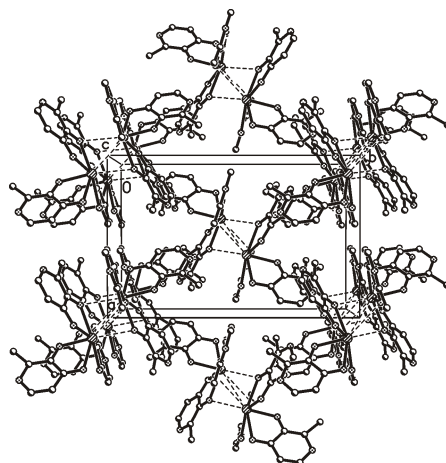


Figure 4. Packing diagram in the unit cell of tris(3-hydroxy-2-methyl-4*H*-pyran-4-onato)bismuth(III).

In this paper, we report the synthesis and characterisation of previously unknown tris(3-hydroxy-2-methyl-4*H*-pyran-4-onato)bismuth(III), a rare example of the complexes of hexa-coordinated bismuth(III) with stereoactive lone pair. In crystal packing, molecules of the complex are dimers due to the Bi...Bi and Bi...O contacts.

Experimental Section

General Procedures. Maltol was extracted from needles of *Abies sibirica* Ledeb. and purified according to the published procedure.² The other reagents employed were reagent-grade. IR spectra were recorded on a Specord 75 IR (4000 – 800 cm⁻¹) and on Specord M-82 (800 – 200 cm⁻¹) instruments. UV spectra were recorded on Specord UV/VIS spectrophotometer. ¹H NMR and ¹³C NMR spectra were recorded on the Bruker DPX-400 and AV-400 at 400.13 MHz and 101.61 MHz, respectively, using HMDS as an internal standard. ¹³C NMR spectra were recorded under complete decoupling from protons as well as without decoupling. Spectral assignment in the ¹³C NMR spectrum was carried out based on the 2D correlation diagrams HMBC. The X-ray diffractions studies were carried out on Kuma Diffraction KM-4 diffractometer at room temperature ($\omega/2\theta$ -scan mode, MoK α radiation, graphite monochromator). The crystal structure was solved by direct methods followed by Fourier syntheses with SHELXS-97³⁶ and refined using anisotropic full-matrix least-squares approximation for all non-hydrogen atoms using SHELXL-97³⁶. Hydrogen atoms were placed geometrically. An absorption correction was applied³⁷, $T_{\min} = 0.294$, $T_{\max} = 0.736$. Crystal data collection and details of the structure determination are summarized in Table 3.

General procedure for the preparation of tris(3-hydroxy-2-methyl-4*H*-pyran-4-onato)bismuth(III)

The aqueous solution of maltol (3.78 g, 0.03 mol in 150 ml of water) was added to the stirred suspension of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (5.84 g, 0.01 mol in 50 ml of water). Then the aqueous 2N solution of NaOH was added dropwise to the reaction mixture under constant stirring until pH = 7.5. The mixture was stirred for 20 min, and then allowed to stand for 12 h at 5 – 7 °C. The pale-yellowish residue was filtered off, washed with water and alcohol and dried under reduced pressure. Yield of the product was 5.43 g (93 %). Elemental analysis (%): calcd. for $\text{C}_{18}\text{H}_{15}\text{BiO}_9$: C 37.0; H 2.57; Bi 35.79; found: C 37.67; H 2.86; Bi 35.98. The monocrystals (mp 245 °C) were grown from saturated aqueous solution at 90°C by slow cooling and evaporation of the solvent.

Supplementary Information Available

CCDC 631348 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from Cambridge Crystallographic Data Centre (CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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