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Nonlinear-optical bis(3-hydroxy-2-methyl-4*H*-pyran-4-onato) complexes of metals

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Electroneutral bis(3-hydroxy-2-methyl-4*H*-pyran-4-onato) complexes of calcium, cadmium and lead showing nonlinear-optical properties have been originally synthesised and characterised by IR, UV and NMR spectroscopy.

3-Hydroxy-2-methyl-4-pyrone (maltol) is a naturally occurring compound.[1–3] A source of maltol is the needles of Siberian fir *Abies sibirica* Ledeb.[4,5] The yield of the extracted target compound is 1.5–2%.[5]

The nonlinear-optical properties of maltol[6] make this chelate lignand[7–9] with intramolecular charge transfer an attractive building block for the design of various metal complexes – new nonlinear-optical media having controlled physical and chemical characteristics.[10,11]

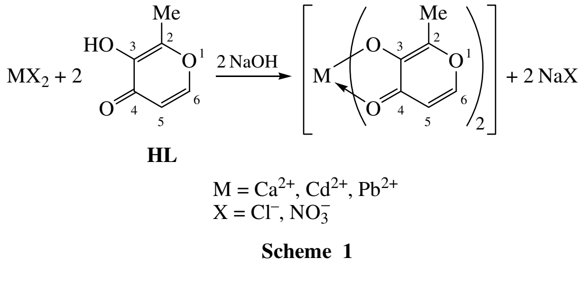
The aim of this work was to synthesise and structurally characterise the first metal complexes of maltol having nonlinear-optical properties.

Maltol reacts with metal ions due to the presence of two functional moieties in its γ-pyrone ring, namely, the C=O group in the 4-position, where the oxygen atom shows electron-donating properties, and the OH group in the 3-position, which is capable to form a salt-like bond with metal ions.

It is evident that in the latter case the maltol coordination should be favoured by its ionization at the O–H bond to form the singly-charged anion of maltol $C_6H_5O_3^-$ (L). Therefore, the reaction was performed in the presence of an alkali (2 N NaOH), which aided to maltol ionization (pK_a 8.6 in water) and neutralised the acid releasing during the reaction. As a result, the reaction equilibrium was shifted towards the formation of the target product (Scheme 1).

The synthesis conditions were optimised to obtain the reaction products in good yields (55–87%).

According to elemental analysis data, the complexes obtained have a stoichiometric metal-to-ligand ratio of 1:2; the complexes of cadmium and calcium contain crystallization water (two and five molecules per molecule of the complex, respectively).[†]



M = Ca^{2+}, Cd^{2+}, Pb^{2+}
X = Cl^-, NO_3^-

Scheme 1

The formation of complexes is accompanied by a batochromic shift of the π→π* transfer band (shift of maximum at 270 nm towards the region of 310–320 nm) in their electronic spectra, as compared to the spectrum of maltol (Figure 1). This fact is attributable to the change in the ligand electron density distribu-

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[†] Maltol was extracted from the needles of *Abies sibirica* Ledeb. and purified according to the published procedure.[9] The reagents [$CaCl_2$, $Pb(NO_3)_2$ and $Cd(NO_3)_2 \cdot 4H_2O$] were of reagent grade.

The IR spectra were recorded on a Specord 75 IR spectrophotometer in the region 4000–800 cm^{-1} (KBr and Vaseline oil) and on a Specord M82 instrument at 800–200 cm^{-1} (Vaseline oil).

The electron absorption spectra were measured on a SF-26 spectrophotometer in the range 240–360 nm (in H_2O; C_M 1×10^{-4}).

The ^{1}H and ^{13}C NMR spectra were recorded on Bruker DPX-400 and AV-400 instruments ($CDCl_3$) with internal stabilization on deuterium (400.13 MHz for ^{1}H, 100.61 MHz for ^{13}C). Chemical shifts δ for ^{1}H and ^{13}C are referred to TMS. The ^{13}C NMR spectra were measured under complete decoupling from protons, as well as without decoupling. Spectral assignment in the ^{13}C NMR spectrum was carried out based on the 2D correlation diagrams HMBC.

Generation of a second harmonica was studied by a powder method[30] under the action of neodymium laser radiation on YAG at 1064 nm, operating in the Q-switching mode. The power density of excitation radiation pulses was 10^8 W cm^{-2}. Radiation spectrum of the second harmonica of the compounds studied was recorded on laboratory optical spectrometer; the measurement error did not exceed 1 nm.

Preparation of metal complexes. A solution of an inorganic metal salt (10 mmol) in water (50 ml) was added to a solution of maltol (2.52 g, 20 mmol) in water (150 ml). The reaction mixture was added dropwise with stirring to 2 N NaOH until the value of pH became constant (8.3–8.9). The precipitation of a flake-like complex was observed. The mixture was stirred for 15–20 min and then allowed to stand at 5–10 °C for 12 h. The precipitate formed was filtered off, washed with water and ethanol, and dried under reduced pressure.

*Bis(3-hydroxy-2-methyl-4*H*-pyran-4-onato)lead(II)*: yield 71%, white crystals, mp 210 °C. Found (%): C, 31.80; H, 2.10; Pb, 45.60. Calc. for $[Pb(C_6H_5O_3)_2]$ (%): C, 31.50; H, 2.20; Pb, 45.32.

*Bis(3-hydroxy-2-methyl-4*H*-pyran-4-onato)cadmium(II) dihydrate:* yield 81%, white crystals, mp 280 °C. Found (%): C, 37.34; H, 3.29; Cd, 27.95. Calc. for $[Cd(C_6H_5O_3)_2]\cdot 2H_2O$ (%): C, 37.14; H, 3.51; Cd, 28.20.

*Bis(3-hydroxy-2-methyl-4*H*-pyran-4-onato)calcium(II) pentahydrate:* yield 56%, white crystals, mp 275 °C. Found (%): C, 37.81; H, 5.32; Ca, 10.35. Calc. for $[Ca(C_6H_5O_3)_2]\cdot 5H_2O$ (%): C, 37.80; H, 5.26; Ca, 10.50.

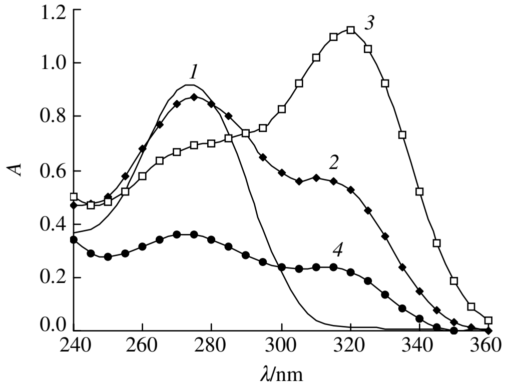

Figure 1 UV spectra of (*1*) maltol, (*2*) $CdL_2 \cdot 2H_2O$, (*3*) $CaL_2 \cdot 5H_2O$ and (*4*) PbL_2.

tion, *i.e.*, to the shift of π electrons across the conjugated chain (polarization) under maltol ionization involving chelate formation,[12] which leads to a decrease in the energy of excitation, as well as to a long-wave shift of the absorption band observed.

The fact that maltol is bound to a metal ion through the oxygen atom of the carbonyl group is confirmed by a decrease of the stretching vibration frequency ($\nu_{C=O}$) by 40–50 cm^{-1} in the IR spectra of the complexes, as compared to the spectrum of a free lignand (Table 1).[7,8] The disappearance of an absorption band (ν_{O-H}) at 3240 cm^{-1}, related to the maltol hydroxyl, is indicative of the hydroxyl group deprotonation followed by the formation of a bond with a metal ion. The presence of bands in the regions 400–460 and 230–270 cm^{-1} may indicate the presence of a metal–oxygen bond.[7,8] Redistribution of electron density in chelates results in a shift of absorption bands, which corresponds to conjugated double bonds of γ-pyrone ($\nu_{C=C}$), to a low-frequency region (Table 1).[7,8] The presence of hydrated water molecules in the complexes of Cd^{II} and Ca^{II} is responsible for the appearance of a wide absorption band in the IR spectra of chelates at 3400–3470 cm^{-1}.

Table 1 Characteristic frequencies (ν/cm^{-1}) in the IR spectra of maltol and its metal complexes.

Compound	Assignment				
	C=O	C=C	M–O	O–H	H_2O
HL	1660	1625		3240	
		1565			
PbL_2	1600	1565	426		
		1500	255		
$CdL_2 \cdot 2H_2O$	1610	1575	436		3450
		1515	235		
$CaL_2 \cdot 5H_2O$	1615	1580	425		3395
		1523	265		

The ^{1}H NMR spectra (Table 2) provide support for the involvement of the maltol hydroxyl proton in the reaction: in the spectra of metal derivatives, a resonance signal at 7.31 ppm caused by maltol hydroxyl proton is absent. In addition, the resonance signal shifts of the protons H-5 and H-6, as well as the methyl group, with respect to their positions in maltol also point to the redistribution of ligand electron density in the molecules of complexes. The signals of H-5 and H-6 protons are observed as doublets with the coupling constant $^3J_{HH}$ 5.0–5.5 Hz, while the signal of the Me protons is singlet.

A comparative analysis of the ^{13}C NMR spectra of maltol and its lead derivative (Table 3) (low solubility of calcium and lead did not allow us to record their ^{13}C NMR spectra) also proves the formation of chelate compounds. The complex formation with Pb^{2+} ions involves the partial deshielding of the ligand carbon atoms, which leads to the observed shift of signals towards a low field, except for C-6. Usually, the deshielding effect impacts on the chemical shifts of C-4, C-3 and C-2 atoms, which are located nearly to the coordination centre. To assign carbon signals, the ^{13}C NMR spectra without decoupling from protons, as well as two-dimensional (2D) HMBC ^{1}H–^{13}C spectra, were recorded. The coupling constants $^1J_{CH}$ of the C-6 atom are higher than those of the C-5 atom. This can be explained by the neighbourhood of the C-6 atom with the oxygen atom.

Table 2 ^{1}H NMR chemical shifts (δ/ppm) and coupling constants (*J*/Hz) of maltol and its metal complexes.

Compound	H-5 ($^3J_{5,6}$)	H-6 ($^3J_{5,6}$)	Me	OH
HL	6.42 (5.2)	7.70 (5.2)	2.36	7.31
$CaL_2 \cdot 5H_2O$	6.65 (5.0)	7.83 (5.0)	2.44	
$CdL_2 \cdot 2H_2O$	6.41 (5.5)	7.70 (5.5)	2.36	
PbL_2	6.44 (5.2)	7.66 (5.2)	2.42	

Table 3 ^{13}C NMR chemical shifts (δ/ppm) and coupling constants (*J*/Hz) of maltol and its lead complex.

Compound	C-2 ($^2J_{CH}$)	C-3 ($^2J_{CH}$)	C-4 ($^2J_{CH}$, $^3J_{CH}$)	C-5 ($^1J_{CH}$, $^2J_{CH}$)	C-6 ($^1J_{CH}$, $^2J_{CH}$)	Me ($^1J_{CH}$)
HL	149.51	143.44	273.25	113.35	154.22	14.37
	(7.4)	(2.8)	(7.4, 1.2)	(167.9, 8.5)	(199.7, 6.4)	(129.6)
PbL_2	157.27	151.45	177.76	114.84	152.94	15.24
			(7.0, 2.4)	(168.6, 8.6)	(197.2, 6.5)	(130.0)

Using the powder method,[13] we found that the crystals of maltol metal complexes generate second radiation harmonica of neodymium laser (line at 532 nm of 1 nm width, corresponding to measurement error of the spectrometer employed), whose efficiency is comparable with the efficiency of a classical nonlinear-optical material, lithium iodate. Non-linear susceptibilities of lithium iodate, initial maltol and its complexes are of the same order. Nevertheless, the maltol complexes, being nonlinear optical materials, possess important advantages such as high heat resistance and low solubility in water, which is essential for the design of optical devices.

Clearly,[10,11] the availability of nonlinear-optical properties of the complexes prepared results from both the known effect of intramolecular charge transfer and the absence of central symmetry of crystalline package.

Thus, the first metal complexes of maltol showing nonlinear-optical properties have been originally synthesised and characterised by spectral methods.

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