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Alkaline Earth Metal Complexes with the Non-cyclic Oxygen-containing Ligand: 1,3-Bis(2-hydroxyphenyl)-1,3-propanedione

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Abstract

Complexes of alkaline earth metal ions with the oxygen-containing ligand 1,3-bis(2-hydroxyphenyl)-1,3-propanedione ($bhppH_3$) have been synthesized. Conductivity, spectral and thermal measurements indicate a non ionic behaviour for all these complexes. IR spectral data suggest a difference in coordination mode between Mg and the other metals. A molecular structure similar to that found in $Zn(bhppH_2)_2\cdot 2EtOH$ is proposed for the Mg complex.

Introduction

There are few cases of true complexes of alkaline or alkaline earth metal ions and they are generally made with oxygen-containing ligands, either macrocyclic or acyclic. The complexing properties have been studied [1] and some theoretical investigations [2] have been carried out on alkaline earth metal ions with oxygen-containing macrocycles. However, such studies have not been conducted with similar noncyclic ligands because they are not able to compete with crown ethers and cryptands [3]. In only a few cases were the complex stabilities of noncyclic polyethers determined for comparison with the cyclic analogues.

We have already reported an anionic lithium complex with the ligand 1,3-bis(2-hydroxyphenyl)-1,3-propanedione (hereafter $bhppH_3$) [4], which is one of the few examples reported in the literature of a non-organometallic discrete lithium complex. In this paper we report on complexes of alkaline earth metal ions with the same ligand, which exhibit a large range of bond interactions. On the other hand the stabilities of these complexes are unusual with regard to other alkaline earth metal ions and acyclic oxygen-containing ligands.

Experimental

General

IR spectra were obtained on a Beckman IR-20 as KBr pellets. ^1H NMR spectra were obtained on a Brucker WP80SY. Thermal measurements were done on a Rigaku thermoflex system. Conductivity measurements were determined on a CDM-3 Radiometer conductivimeter. The ligand $bhppH_3$ was obtained according to a reported method by a Claisen condensation of 2-hydroxyacetophenone and methyl salycylate [5]. All solvents were reagent grade and used as received.

Synthesis of Compounds $M(bhppH_2)_2\cdot xH_2O$ (M = Mg, Ca, Sr, Ba)

To a warm solution of $bhppH_3$ (2 mmol) in methanol (15 ml), $M(AcO)_2\cdot xH_2O$ (1 mmol) in methanol (M = Mg) or water (2–3 ml) (M = Ca, Sr, Ba) was added with constant stirring. Following the addition, a precipitate separated (M = Mg) or was induced by adding a few drops of water (M = Ca, Sr, Ba). The resulting suspension was stirred at room temperature for an additional 10–15 min period and filtered. The solid was washed with methanol (M = Mg) or ether (M = Ca, Sr, Ba) and dried under vacuum. Yields were about 60–70%. *Anal.* For M = Mg. Found: C, 63.4; H, 4.6. Calc. for $C_{30}H_{26}MgO_{10}$: C, 63.12; H, 4.56%. For M = Ca. Found: C, 59.1; H, 4.6. Calc. for $C_{30}H_{28}CaO_{11}$: C, 59.59; H, 4.63%. For M = Sr. Found: C, 53.6; H, 4.5. Calc. for $C_{30}H_{30}SrO_{12}$: C, 53.72; H, 4.47%. For M = Ba. Found: C, 52.6; H, 4.3. Calc. for $C_{30}H_{26}BaO_{10}$: C, 52.69; H, 3.83%.

Synthesis of $Na(bhppH_2)\cdot H_2O$

We reported the synthesis of this compound previously [4]. However the following preparation is much easier and more straightforward.

To a solution of $bhppH_3$ (1 mmol) in methanol (15 ml) NaMeO (1 mmol) was added with constant stirring. Upon the addition, a yellow solid separated, which was filtered, washed with methanol and dried under vacuum. Yield 60%. *Anal.* Found: C,

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60.1; H, 4.3. Calc. for $C_{15}H_{13}NaO_5$: C, 60.8; H, 4.39%.

Synthesis of Compound Ni(MeSalen) Ca(bhppH$_2$)$_2$

To a refluxing solution of Ni(MeSalen) [6] (0.176 g, 0.5 mmol) (MeSalen = *N,N'*-ethylenebis(2-hydroxyacetophenoneimine) in CH_2Cl_2 (20 ml) maintained under N_2 atmosphere, anhydrous Ca(bhppH$_2$)$_2$ (0.275 g, 0.5 mmol) was added and the resulting solution was refluxed for 1 h. After that time, the mixture was cooled to room temperature and an orange solid began to precipitate. The solid was filtered, washed with CH_2Cl_2 and dried under vacuum. Yield 40%. The anhydrous Ca(bhppH$_2$)$_2$ was obtained from Ca(bhppH$_2$)$_2$·3H$_2$O, after heating it for several hours at 120 °C in an oven. *Anal.* Found: C, 64.0; H, 4.4; N, 3.3. Calc. for $C_{48}H_{40}CaN_2NiO_{10}$: C, 63.80; H, 4.40; N, 3.26%.

Results

^{1}H NMR of Compounds M(bhppH$_2$)$_2$·xH$_2$O (M = Mg, Ca, Sr, Ba) and Na(bhppH$_2$)·H$_2$O

^{1}H NMR was used as a technique to identify the nature of the solvent molecules, which could be either water or methanol. This was a necessary step prior to the interpretation of the thermogravimetric data, since the analytical results were not clear enough to permit the distinction. In addition, some structural information about these compounds was obtained which correlated very well with the IR data.

These spectra display in d$_6$-DMSO (M = Na, Mg, Ba) or CD_3OD (M = Ca, Sr) three groups of bands corresponding to the aromatic and methinic protons near 6.8, 7.3, and 7.9 ppm with relative intensities 2:2:2.5, respectively, and another absorption at 12.5 –14 ppm corresponding to the phenylic protons. In none of these spectra were bands attributable to methanol observed. On the other hand, each of the ^{1}H NMR spectra of the Ca and Sr compounds in d$_6$-DMSO presented a complicated group of bands in the range 15–13, 9–6 and 4–2.5 ppm, due to a mixture of compounds. Comparison of these spectra with those of the same compounds in CD_3OD clearly proves that there has been a chemical interaction between M(bhppH$_2$)$_2$·xH_2O (M = Ca, Sr) and DMSO. This fact is evidence of a difference in behaviour of the Ca and Sr compounds against that of Na, Mg and Ba towards DMSO, which can only be interpreted in terms of a different coordination of the ligand and the water molecules about the metal ion.

Studying more closely the three groups of absorptions near 6.8, 7.3 and 7.9 ppm it is possible to observe slight variations in the position of the band at 7.9 ppm as a function of the metal ion. The Mg compound shows this band at 8.1 ppm, 0.2 ppm higher than the remaining compounds. Even though this shift is small, it seems to have some structural significance since this is the same position at which a corresponding signal is observed in clearly chelated compounds of the same ligand such as Zn(bhppH$_2$)$_2$·2EtOH and NEt$_4$Li(bhppH$_2$)$_2$, whose molecular structure has been solved by X-ray diffraction methods [4, 7].

IR Spectroscopy of Compounds M(bhppH$_2$)$_2$·xH$_2$O (M = Mg, Ca, Sr, Ba) and Na(bhppH$_2$)·H$_2$O

The IR spectra show important discordances in the carbonyl region as a function of the metal ion (see Fig. 1). The remainder of the spectrum is very similar except in the hydroxilic region where the intensity of the water absorptions varies from one compound to another. The Mg compound shows two sharp absorptions at 1590 and 1620 cm^{-1}, as is observed in NEt$_4$Li(bhppH$_2$)$_2$ and M(bhppH$_2$)$_2$·xROH (M = Mn, Co, Ni, Cu, Zn, Cd). On the other hand, the Na, Ca, Sr and Ba complexes show only one broader absorption at 1600 cm^{-1}.

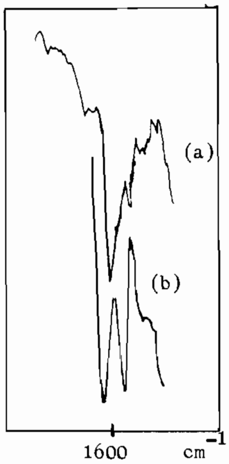

Fig. 1. IR spectra in the carbonyl region. (a) M(bhppH$_2$)$_2$·xH$_2$O M = Ca, Sr, Ba and (b) Mg(bhppH$_2$)$_2$·2H$_2$O.

Conductivity Data

Measurements were made at 25 °C at 10^{-3} M concentration in purified methanol. Molar conductivity values were almost 20 ohm^{-1} cm^2 mol^{-1} (M = Mg, Ca, Sr, Ba) and 70 ohm^{-1} cm^2 mol^{-1} (M = Na). A conductivity test was carried on Me$_3$NHCl giving a value of 84 ohm^{-1} cm^2 mol^{-1}. These values are in agreement with those expected for non-electrolytes (M = Mg, Ca, Sr, Ba) and slightly low for 1:1 electrolytes (M = Na). According to the literature, values close to 80–115 and 160–220 ohm^{-1} cm^2 mol^{-1} are expected for 1:1 and 1:2 electrolytes [8].

TABLE I. Thermal Data for $M(bhppH_2)_2 \cdot xH_2O$ Complexes

Complex	Molecular weight	T_1^i (°C)[a]	$m\%$ (exp)[b]	$m\%$ (calc)[b]	T_2^i (°C)[a]
$Mg(bhppH_2)_2 \cdot 2H_2O$	571	145	6.50	6.31	238
$Ca(bhppH_2)_2 \cdot 3H_2O$	604	135	8.79	8.34	178
$Sr(bhppH_2)_2 \cdot 4H_2O$	652	116	11.04	10.75	188
$Ba(bhppH_2)_2 \cdot 2H_2O$	684	85	4.69	5.26	185
$Na(bhppH_2) \cdot H_2O$	296	100	5.6	6.08	175

[a] T_1^i and T_2^i: initiation temperatures for the first and second weight losses, respectively. [b] $m\%$: weight loss percentage.

Thermal Analyses

The results of thermal analyses are reported in Table I. All the compounds undergo an initial reaction with initiation temperatures T_1^i ranging from 85–145 °C (2 °C/min), depending upon the metal, with loss of the solvation water molecules.

$$M(bhppH_2)_2 \cdot xH_2O \longrightarrow M(bhppH_2)_2 + xH_2O$$

The second mass loss observed in the TG curves is common for all complexes with observed T_2^i values of 175–240 °C (2 °C/min). The identification of 2-(2′-hydroxyphenyl)flavone in the sample pan has been a common fact in all these experiments, as has been observed in transition metal complexes of $bhppH_3$ [9].

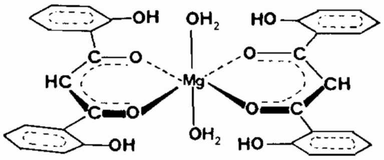

Fig. 2. Proposed structure for $Mg(bhppH_2)_2 \cdot 2H_2O$.

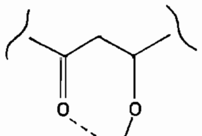

Fig. 3. Schematic representation of the bonding mode about the Ca, Sr and Ba complexes.

Discussion

The reaction of $bhppH_3$ with alkaline earth metal acetates in methanol yields compounds with the molecular formulae $M(bhppH_2)_2 \cdot xH_2O$ (M = Mg, x = 2; M = Ca, x = 3; M = Sr, x = 4; M = Ba, x = 2). The reaction with NaAcO yields $Na(bhppH_2) \cdot H_2O$.

Even though the $bhppH_2$–alkaline earth metal compounds have similar stoichiometry regardless of the number of water molecules, it is obvious from the spectroscopic data in the IR carbonyl region (see Fig. 1) that the strength of the metal-to-$bhppH_3$ ligand depends on the nature of the metal; however, the low conductivity values indicate a non-ionic behaviour for all $M(bhppH_2)_2 \cdot xH_2O$ compounds and a 1:1 ionic type for the complex $Na(bhppH_2) \cdot H_2O$ in solution.

Because of the closeness of the IR and ^1H NMR spectra of the $Mg(bhppH_2)_2 \cdot 2H_2O$ with those of $Zn(bhppH_2)_2 \cdot 2EtOH$ and $NEt_4Li(bhppH_2)_2$, and the high water elimination temperature for $Mg(bhppH_2)_2 \cdot 2H_2O$, which seems to favour strong M–OH bonds, we propose for the Mg compound a structure similar to that found in $Zn(bhppH_2)_2 \cdot 2EtOH$ [7] (Fig. 2).

Even though the remaining alkaline-earth compounds behave as non-ionic species, we believe that in these compounds the β-diketone moiety does not bite the metal in the same fashion as it does in $Mg(bhppH_2)_2 \cdot 2H_2O$, as evidenced by the IR findings. May-be a binding mode such as that depicted in Fig. 3, with unequal M–O bonds would be more consistent with the experimental data, particularly with the IR spectra which resemble that of the free ligand, especially in the CO region.

The strength dependence of the C=O···M bond with regard to the nature of the metal atom would be an explanation for the strange difference in behaviour between the Ba compounds and the Ca and Sr compounds toward DMSO, as evidenced by the ^1H NMR data.

When anhydrous $Ca(bhppH_2)_2$ is allowed to interact with Ni(MeSalen), a compound with analysis corresponding to stoichiometry $Ni(MeSalen)Ca(bhppH_2)_2$ is obtained. This is a clear proof of the tendency of calcium to fill its coordination sphere. The reaction did not proceed when hydrated $Ca(bhppH_2)_2 \cdot 3H_2O$ was used; we have also encountered great difficulty in removing the water molecules in $Ca(bhppH_2)_2 \cdot 3H_2O$ (120 °C, 24 h) compared to $Zn(bhppH_2)_2 \cdot 2H_2O$ (120 °C, 15 min). It is important to notice these facts since they corroborate our point of view about the formation of alkaline earth complexes with the ligand $bhppH_3$.

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