Thermochimica Acta, 79 (1984) 315–321
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THE PREPARATION AND THERMAL ANALYSIS STUDIES OF COBALT AND ZINC 1,3-BIS-(2-HYDROXYPHENYL)-1,3-PROPANDIONE ALCOHOL COMPLEXES

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(Received 9 April 1984)

ABSTRACT

The dependence of the M–O (alcohol) bond in 1,3-bis-(2-hydroxyphenyl)-1,3-propandione alcohol complexes with increasing R (alcohol) groups has been studied by means of DTA, TG and UV–visible analyses. The enthalpy of the alcohol–metal breaking process is nearly constant indicating a negligible dependence of the M–O (alcohol) bond with the bulkiness of the R (alcohol) group. Because of this independence a bonded alcohol is easily replaced in solution by another appropriate oxygen-donor molecule present in the medium at a larger concentration.

INTRODUCTION

In previous papers [1,2] the syntheses of several 1,3-bis-(2-hydroxyphenyl)-1,3-propandione ($bhppH_3$) complexes with general formulae $M(bhppH_2)_2 \cdot S,S'$ (M = Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Pd(II); S,S′ = solvent molecules) were reported. The molecular structure of $Zn(bhppH_2) \cdot 2\ CH_3CH_2OH$ was proved to be a tetragonally distorted octahedron with its two β-diketone moities occupying the equatorial positions while the two axial positions were occupied by the O-bonded ethanols [3]. The easy replacement of the bonded methanol molecules (S,S′) by ethanol, when the zinc–methanol complex was dissolved in ethanol, prompted the study of the effect of the alcohol size in the ease of alcohol removal in zinc complexes. However, attempts to introduce alcohols larger than ethanol did not succeed. Better results were obtained with cobalt complexes where a larger variety of alcohols were introduced. Solid-state thermal analysis and UV–visible spectroscopy are sound techniques for gaining information on

0040-6031/84/$03.00

the bonding in complexes [4,5]. These techniques have been used in this paper to study several cobalt and zinc alcohol complexes and the differences observed upon the size of the alcohol. In addition, the syntheses of these complexes of general formulae Co(bhppH_2)S,S′ (S,S′ = H_2O, CH_3OH, CH_3CH_2OH, $CH_3CH_2CH_2OH$, $CH_3CH_2CH_2CH_2OH$) are reported.

EXPERIMENTAL

Preparation of compounds

The ligand bhppH_3 was prepared by methods previously reported [6]. All reagents and solvents were reagent grade and were used as received.

Synthesis of Co(bhppH$_2$)$_2$ · 2 H$_2$O

To a flask containing 0.256 g (1 mmol) of bhppH_3 in 12 cm^3 of refluxing isopropanol was added a hot solution of 0.145 g (0.5 mmol) of $Co(NO_3)_2 \cdot 6\ H_2O$ in 10 cm^3 of the same solvent. The solution acquired a reddish color and, upon the slow addition of five drops of aqueous ammonia (25%), a yellow-orange solid separated which was filtered and washed with isopropanol, ethanol and ether. The solid was stored in a desiccator containing $CaCl_2$. Yield: 93%. Analysis, calcd. for $CoC_{30}H_{26}O_{10}$: C, 59.51; H, 4.30; found: C, 59.75; H, 4.42.

Synthesis of Co(bhppH$_2$)$_2$ · 2 CH$_3$OH

To a flask containing 0.256 g (1 mmol) of bhppH_3 in 20 cm^3 of refluxing methanol was added a hot solution of 0.124 g (0.5 mmol) of $Co(CH_3COO)_2 \cdot 4\ H_2O$ in 10 cm^3 of the same solvent. Upon cooling a yellow-orange solid precipitated which was filtered and washed with methanol and ether. The solid was stored in a desiccator containing $CaCl_2$. Yield: 92%. Analysis, calcd. for $CoC_{32}H_{30}O_{10}$: C, 60.67; H, 4.74; found: C, 60.28; H, 4.91.

Synthesis of Co(bhppH$_2$)$_2$ · 2 CH$_3$CH$_2$OH

The synthesis was performed as previously reported [2]. It was essentially the same as for the methanol complex, using ethanol instead of methanol. Yield: 72%. Analysis, calcd. for $CoC_{34}H_{34}O_{10}$: C, 61.73; H, 5.14; found: C, 61.76; H, 5.21.

Synthesis of Co(bhppH$_2$)$_2$ · CH$_3$CH$_2$CH$_2$OH · H$_2$O

Two solutions containing 0.256 g (1 mmol) of bhppH_3 in 20 cm^3 of *n*-propanol (Merck 0.05% H_2O), and 0.124 g (0.5 mmol) of $Co(CH_3COO)_2 \cdot 4\ H_2O$, respectively, were mixed at 0 °C. The solution was kept refrigerated at −15 °C for three days and the resulting solid was filtered and stored in a desiccator containing $CaCl_2$. Yield: 70%. Analysis, calcd. for $CoC_{33}H_{32}O_{10}$: C, 61.21; H, 4.95; found: C, 61.68; H, 5.15.

Synthesis of $Co(bhppH_2)_2 \cdot 2\ CH_3CH_2CH_2CH_2OH$

The same procedure as in the previous synthesis was used. Yield: 88%. Analysis, calcd. for $CoC_{38}H_{42}O_{10}$: C, 63.6; H, 5.86; found: C, 63.34; H, 6.09.

Synthesis of $Zn(bhppH_2)_2 \cdot 2\ CH_3CH_2OH$

The synthesis was performed as previously reported [2]. It was essentially the same as for the methanol–cobalt complex using $Zn(CH_3COO)_2 \cdot 2\ H_2O$ and ethanol.

Synthesis of $Zn(bhppH_2)_2$

The $Zn(bhppH_2)_2 \cdot 2\ CH_3CH_2OH$ was placed in an oven at 110 °C for 30 min yielding $Zn(bhppH_2)_2$.

Thermal measurements

Simultaneous differential thermal analysis (DTA) and thermogravimetry (TG) were carried out in air atmosphere on ~ 50-mg (powdered) samples at heating rates of 5 and 0.2 °C min^{-1} using an STA 429 Netzsch thermal analyzer. Differential scanning calorimetry (DSC) studies were carried out using a Perkin-Elmer DSC-2, in an argon atmosphere, on ~ 5-mg samples at a heating rate of 5 °C min^{-1}. Sample pans with a pin hole were used in the last case.

RESULTS AND DISCUSSION

Synthesis and characterization of complexes

Reaction of 1,3-bis-(2-hydroxyphenyl)-1,3-propandione ($bhppH_3$) with $Co(CH_3COO)_2 \cdot 4\ H_2O$ or $Zn(CH_3COO)_2 \cdot 2\ H_2O$, in the appropriate alcohol, yields $Co(bhppH_2)_2S,S'$ as indicated in Table 1. See eqn. (1) for S,S′ = methanol.

$$Co(CH_3COO)_2 \cdot 4\ H_2O + 2\ bhppH_3 + 2\ CH_3OH \xrightarrow[CH_3OH]{} Co(bhppH_2)_2 \cdot 2\ CH_3OH + 2\ CH_3COOH + 4\ H_2O \qquad (1)$$

Care must be taken when the larger alcohols, *n*-propanol and *n*-butanol, are introduced because an alcohol substitution by water readily takes place. It is assumed that processes like these are the reason why zinc complexes with larger alcohols could not be isolated. The cobalt–water complex may be obtained using $Co(NO_3)_2 \cdot 6\ H_2O$ in isopropanol, or by allowing total substitution of *n*-propanol or *n*-butanol complexes by water as mentioned earlier. All the alcohol complexes have almost undistinguishable IR spectra

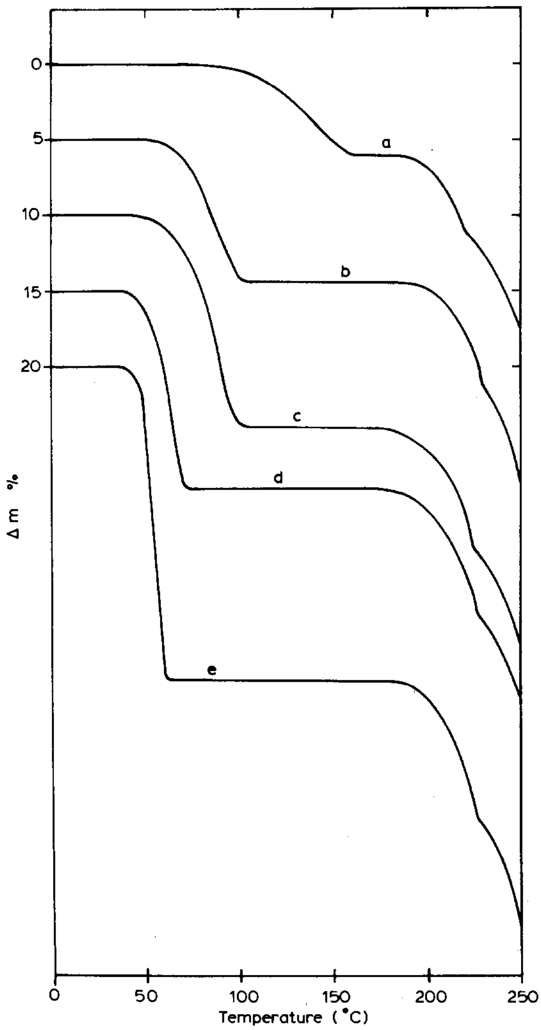


Fig. 1. TG curves at 0.2 °C min^{-1}: a, Co(bhppH$_2$)$_2$·2 H$_2$O; b, Co(bhppH$_2$)$_2$·2 MeOH; c, Co(bhppH$_2$)$_2$·2 EtOH; d, Co(bhppH$_2$)$_2$·*n*-PrOH·H$_2$O; e, Co(bhppH$_2$)$_2$·2 *n*-BuOH.

which promote the assumption of a Co/Zn octahedral coordination, as in Zn(bhppH$_2$)$_2$ · 2 CH$_3$CH$_2$OH. The analytical data are consistent with the number of solvent molecules as they are also corroborated by TG measurements.

Thermal and spectral measurements

The results of the TG studies are given in Figs. 1 and 2, and Table 1. All these complexes, including zinc, undergo a first endothermic reaction with initiation temperatures T_1^i (0.2 °C min^{-1}) ranging from 37 to 68 °C, depend-

TABLE 1

Thermogravimetric and enthalpic data for cobalt and zinc alcohol complexes

Complex	1st weight loss					2nd weight loss		
	Molecular weight	T_1^i (°C)	Δm%(exp)	Δm%(calc)	ΔH(kcal mol^{-1})	T_2^i (°C)	Δm%(exp)	Δm%(calc)[a]
$Co(bhppH_2)_2 \cdot 2\ H_2O$	607	68	5.7	5.93	27.2	180	5.2	2.96
$Co(bhppH_2)_2 \cdot 2$ MeOH	635	46	9.1	10.07	25.3	181	6.2	2.83
$Co(bhppH_2)_2 \cdot 2$ EtOH	663	49	13.64	13.87	29.7	174	8.1	2.71
$Co(bhppH_2)_2 \cdot$ *n*-PrOH $\cdot H_2O$	649	37	12.5	12.01	30.0	159	5.2	2.77
$Co(bhppH_2)_2 \cdot 2$ *n*-BuOH	719	57	20.9	20.6	30.8	186	7.5	2.50
$Zn(bhppH_2)_2$	577	–	–	–	–	165	8.3	3.12
$Zn(bhppH_2)_2 \cdot 2$ EtOH	669	50	13.9	13.75	15	160	5.3	2.69

[a] Calculated for one water molecule per molecular unit of the starting complex.

ing upon the alcohol, with loss of the two solvation molecules

$$Co(bhppH_2)_2 \cdot 2\ ROH \rightarrow Co(bhppH_2)_2 + 2\ ROH \qquad (2)$$

No apparent relationship was found between the different T_1^i values and the size of the solvating alcohols. However, as may be seen from Fig. 1, the reaction time decreases as the size of the alcohol increases. The observed reaction times at 0.2°C min^{-1} are: aquo, 450; methanol, 285; ethanol, 255; propanol, 165 and butanol, 100 min. The enthalpy values for these processes are very similar (~ 30 kcal mol^{-1}) increasing slightly with the size of the alcohol. If this enthalpy value is thought of as two terms: the bonding energy and the energy necessary to remove the solvating molecule from the boundaries of the crystal, it seems logical, upon examination of Table 1, to consider that the first term, which is the larger, is very similar in all the complexes, and that the small variations observed in the ΔH values are due to the effect of the size variations of the alcohols.

The values of the bonding energies are in good agreement with the ease of alcohol substitution observed in the zinc and cobalt complexes, as evidenced by the UV—visible spectra of the alcohol solvated cobalt complexes in THF (tetrahydrofuran) solution, where substitution of the solvating molecules by O-bonded THFs occur

$$Co(bhppH_2)_2 \cdot 2\ ROH + 2\ THF \xrightarrow[THF]{} Co(bhppH_2)_2 \cdot 2\ THF + 2\ ROH \qquad (3)$$

An identical spectrum is observed when the non-solvated complex

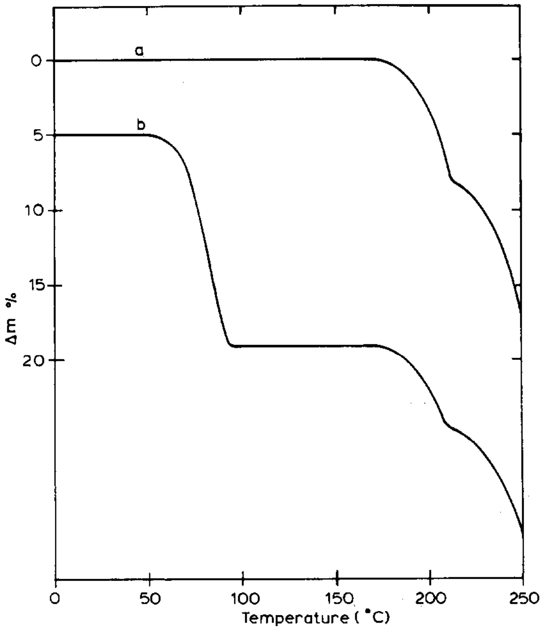
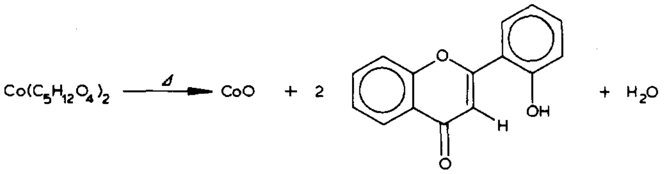


Fig. 2. TG curves at 0.2°C min^{-1}: a, $Zn(bhppH_2)_2$; b, $Zn(bhppH_2)_2 \cdot 2$ EtOH.

$Co(bhppH_2)_2$ is dissolved in THF clearly indicating that the color of the solution is due to $Co(bhppH_2)_2 \cdot 2$ THF and not to $Co(bhppH_2)_2 \cdot 2$ ROH. The spectrum of $Co(bhppH_2)_2 \cdot 2\ CH_3CH_2CH_2CH_2OH$ in butanol displays a shoulder at 655 nm, while in THF this is observed at 645 nm. As a consequence of the similarity in the bonding energy, substitution readily takes place when another appropriate O-donor molecule is present at a much larger concentration, the difference in concentration being the driving force of the process.

The second mass loss observed in the TG curves is common for all complexes with observed T_2^i values at ~ 180 °C at 0.2 °C min^{-1}. The identification of 2-(2′-hydroxyphenyl)flavone, by comparison with an authentic sample, in the walls of the TG chamber indicate that the process taking place is the dehydration of $bhppH_2$ yielding water, 2-(2′-hydroxyphenyl)flavone, and cobalt oxide (eqn. 4).



(4)

The high melting point of this flavone (252 °C) should explain why the mass loss is larger than that corresponding to one molecule of water, but smaller to that expected for two flavone and one water molecule per molecular unit of the cobalt complex. At this stage the complex is decomposed and no attempts were made to study the subsequent decomposition processes.

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