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Alkaline and Alkaline Earth Dinuclear Metal Complex Derivatives of *N*,*N*′-Ethylenebis(2-hydroxyacetophenoneimine) (mesalen) and 1,3-Bis-(2-hydroxyphenyl)-1,3-propanedione (bhppH$_3$)

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Abstract

The copper and nickel complexes of mesalen (mesalen = *N*,*N*′-ethylenebis(2-hydroxyacetophenoneimine) have been used as ligands to form binuclear or trinuclear complexes with bis(1,3-bis(2-hydroxyphenyl)-1,3-propanedionate)metal(II) complexes, M′(bhppH$_2$)$_2$, where M′ = Mg, Ca, Sr and Ba. Similar dinuclear complexes have been obtained with lithium starting from LiMeO. The stoichiometries differ as a result of their charge M(mesalen)Li(bhppH$_2$) or their ionic/covalent radius. For Mg(II), Ca(II) and Sr(II) the stoichiometry is M(mesalen)M′(bhppH$_2$)$_2$ and for Ba(II) the observed stoichiometry is [M(mesalen)]$_2$M′(bhppH$_2$)$_2$. IR spectral data suggest a difference in coordination mode between the Li/Mg compounds *versus* the other alkaline earth metal complexes. A molecular structure similar to that found in Cu(mesalen)Zn(bhppH$_2$)$_2$ is proposed for the Mg, Ca and Sr compounds.

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. These complexes have recently raised a special interest as shown by the number of papers being published about this subject [1, 2]. These are significant in the areas of bioinorganic chemistry and complex formation in solution. The ligands that have been used to carry on these studies are mainly based on alcohols, phenols and organic acids but in no case, to our knowledge, has a complex been used as a ligand.

We have already reported an anionic lithium complex [3] with the ligand 1,3-bis(2-hydroxyphenyl)-1,3-propanedione (hereafter bhppH$_3$), and a series of alkaline earth metal complexes with this same ligand [4]. Recently, we published a paper closely related to the present matter, but with only transition metals [5]. It consisted of the synthesis and physical properties of dinuclear MM′ transition metal complexes with the same ligands used here and with molecular formulas M(mesalen)M′(bhppH$_2$)$_2$. The crystal and molecular structure of Cu(mesalen)Zn(bhppH$_2$)$_2$ was reported. The fact that we had obtained these dinuclear compounds as well as the lithium and alkaline earth complexes impelled us to see if it was possible to get similar dinuclear compounds but with transition and alkaline-earth metal ions. This paper concentrates on the synthesis and proposed structures of these type of complexes. The stoichiometries differ as a result of their charge M(mesalen)Li(bhppH$_2$) or their ionic/covalent radius. For Mg(II), Ca(II) and Sr(II) the stoichiometry is M(mesalen)M′(bhppH$_2$)$_2$ and for Ba(II) the observed stoichiometry is [M(mesalen)]$_2$M′(bhppH$_2$)$_2$.

Experimental

General

The ligand 1,3-bis(2-hydroxyphenyl)-1,3-propanedione (bhppH$_3$) was obtained according to a reported method [6] by a Claisen condensation of 2-hydroxyacetophenone and methyl salycylate. M(mesalen) (M = Cu, Ni; mesalen = *N*,*N*′-ethylenebis(2-hydroxyacetophenoneimine)) was obtained according to a procedure reported by Sinn *et al.* [7]. M′(bhppH$_2$)$_2$·xH$_2$O were obtained following the procedure indicated in ref. 4. CH$_2$Cl$_2$ was dried with molecular sieves before use. All other solvents were reagent grade and were used as received. Elemental analyses of the newly prepared complexes were performed in our microanalytical laboratory using a Perkin-Elmer 240 microanalyzer. Infrared spectra were recorded on a Beckman IR-20A spectrophotometer as KBr pellets.

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Synthesis of Compounds [M(mesalen)]M'(bhppH$_2$)$_2$ (M = Ni, Cu; M' = Mg, Ca, Sr) and [M(mesalen)]$_2$-Ba(bhppH$_2$)$_2$

To a refluxing solution of M(mesalen) (M = Ni, Cu) (0.176 g, 0.5 mmols) in CH_2Cl_2 (20 ml) maintained under N_2 atmosphere, anhydrous M'(bhppH$_2$)$_2$ (0.5 mmol) was added and the resulting solution (M' = Mg, Ca)/suspension (M' = Sr, Ba) was refluxed for 5 h (M' = Mg, Ca, Sr) and 12 h (M' = Ba).

After that time the suspended solid (M' = Sr, Ba) was filtered or allowed to precipitate at room temperature (M' = Mg, Ca) and later filtered. The solid was washed with CH_2Cl_2 and dried under vacuum. Yield 40–50%.

Analysis for [M(mesalen)]M'(bhppH$_2$)$_2$

For M = Ni and M' = Mg. Found: C, 65.08; H, 4.38; N, 3.26. Calc. for $C_{48}H_{40}O_{10}N_2NiMg$: C, 64.94; H, 4.51; N, 3.16%.

For M = Ni and M' = Ca. Found: C, 64.03; H, 4.40; N, 3.30. Calc. for $C_{48}H_{40}O_{10}N_2NiCa$: C, 63.80; H, 4.40; N, 3.26%.

For M = Ni and M' = Sr. Found: C, 60.21; H, 4.28; N, 2.96. Calc. for $C_{48}H_{40}O_{10}N_2NiSr$: C, 60.66; H, 4.24; N, 2.95%.

For M = Cu and M' = Mg. Found: C, 64.53; H, 4.68; N, 3.20. Calc. for $C_{48}H_{40}O_{10}N_2CuMg$: C, 64.58; H, 4.49; N, 3.14%.

For M = Cu and M' = Ca. Found: C, 63.04; H, 4.40; N, 2.98. Calc. for $C_{48}H_{40}O_{10}N_2CuCa$: C, 63.46; H, 4.41; N, 3.08%.

For M = Cu and M' = Sr. Found: C, 60.04; H, 4.22; N, 2.93. Calc. for $C_{48}H_{40}O_{10}N_2CuSr$: C, 60.30; H, 4.19; N, 2.93%.

Analysis for [M(mesalen)]$_2$Ba(bhppH$_2$)$_2$

For M = Ni. Found: C, 58.17; H, 4.53; N, 4.04. Calc. for $C_{66}H_{58}O_{12}N_4Ni_2Ba$; C, 58.55; H, 4.29, N, 4.14%.

For M = Cu. Found: C, 58.49; H, 4.30; N, 4.09. Calc. for $C_{66}H_{58}O_{12}N_4Cu_2Ba$: C, 58.13; H, 4.26; N, 4.11%.

The anhydrous M'(bhppH$_2$)$_2$ were obtained from M'(bhppH$_2$)$_2$·xH$_2$O after heating them according to Table I.

TABLE I. Dehydration Times and Temperatures for M'(bhppH$_2$)$_2$·xH$_2$O

	Temperature (°C)	Time (h)	Vacuum (0.5 torr)
Mg(bhppH$_2$)$_2$·2H$_2$O	130	6	
Ca(bhppH$_2$)$_2$·3H$_2$O	120	6–10	
Sr(bhppH$_2$)$_2$·4H$_2$O	110	4	yes
Ba(bhppH$_2$)$_2$·2H$_2$O	80–90	5	yes

Synthesis of Compounds M(mesalen)Li(bhppH$_2$) (M = Ni, Cu)

To a refluxing solution of M(mesalen) (M = Ni, Cu) (0.32 g, 0.9 mmols) in CH_2Cl_2 (50 ml) maintained under N_2 atmosphere, LiMeO (0.9 mmol) in MeOH (1 ml) was added and the solution left to stir at room temperature for 1 h. After that time bhppH$_3$ (0.23 g, 0.9 mmol) was added and the mixture allowed to stir for an additional 2 h. The resulting solid was filtered and dried under vacuum. Yield 90%.

Analysis.

For M = Ni. Found: C, 64.08; H, 4.78; N, 4.62. Calc. for $C_{33}H_{29}O_6N_2NiLi$: C, 64.42; H, 4.72; N, 4.55%.

For M = Cu. Found: C, 63.54; H, 4.84; N 4.58. Calc. for $C_{33}H_{29}O_6N_2CuLi$: C, 63.92; H, 4.68; N, 4.52%.

Results and Discussion

The reaction of LiMeO/bhppH$_3$, or anhydrous M'(bhppH$_2$)$_2$ (M' = Mg(II), Ca(II), Sr(II), Ba(II)) with M(mesalen) (M = Cu(II), Ni(II)) in CH_2Cl_2 yields heterodinuclear or heterotrinuclear complexes, with the special interest of M' being an alkaline (Li) or alkaline earth metal ion. The general sequence of reactions starting from the M(bhppH$_2$)$_2$·SS' is indicated in Scheme 1.

$$\mathrm{M(bhppH_2)_2\cdot SS'} \xrightarrow{\Delta} \mathrm{M(bhppH_2)_2}$$

$$\mathrm{M(bhppH_2)_2} + x\mathrm{M(mesalen)} \longrightarrow$$

$$[\mathrm{M(mesalen)}]x\mathrm{M'(bhppH_2)_2}$$

$(x = 1, \mathrm{M} = \mathrm{Mg, Ca, Sr}; x = 2, \mathrm{M} = \mathrm{Ba})$

Scheme 1.

As indicated earlier [4, 5], the desolvation reaction is necessary to provide empty positions in the coordination sphere of the M' metal to be occupied by the phenoxy groups of the M(mesalen) moiety.

The stoichiometries differ as a result of their charge M(mesalen)Li(bhppH$_2$) or their ionic/covalent radius. For Mg(II), Ca(II), Sr(II) (all ions with ionic radius $r \leqslant 1.12$) the stoichiometry is M(mesalen)-M'(bhppH$_2$)$_2$ and for Ba(II) ($r = 1.34$) the observed stoichiometry is [M(mesalen)]$_2$Ba(bhppH$_2$)$_2$.

It is interesting to notice the increase of the ion's coordination number as its volume is enlarged. Apparent coordination numbers 4, 6, and 8 are found for Li(I), the series Mg to Sr(II), and Ba(II), respectively. This trend appears to be logical since the larger is the size, the more feasible it is to have a larger number of coordination points. Coordination numbers of 10 are found in some barium compounds such as bis(2-nitrophenolato)barium(II) [8] and 9 in bis(2,4-dinitrophenolato)bis(triethanolamine)-barium(II) [9] and the barium salt of 2,4,6-trinitro-1,3-benzenediol (styphnic acid) monohydrate [10]. In addition a coordination number of 8 is found in several compounds of Ba(II) such as tetraaquabis(1,10-phenanthroline)barium(II) [11] and $Ba[C_5(CO_2Me)_5]_2$ where $[C_5(CO_2Me)_5]$ is the dianion of pentakis(methoxycarbonyl)cyclopentadiene [12].

In these compounds the geometry observed about the barium center is close to a distorted cubic geometry, consequently, we propose for the barium compound presented here a distorted dodecahedral or cubic geometry about the barium atom. Unfortunately, the high insolubility of these compounds has precluded, to date, the growth of crystals suitable for an X-ray diffraction analysis, and consequently, the correct assignment of the structure. For the lithium compound a tetrahedral geometry, similar to that found in $[Li(bhppH_2)_2]^-$ [3] is proposed. For the magnesium calcium and strontium compounds an octahedral geometry about the metal ion, close to that found in $Cu(mesalen)Zn(bhppH_2)_2$ [5] is expected. Lithium and magnesium compounds present an IR comparable to those found in transition metal complexes of $bhppH_3$ (β-diketone region, $\approx$1600 cm^{-1}), which suggests an equivalent M–O (β-diketone) type of bond.

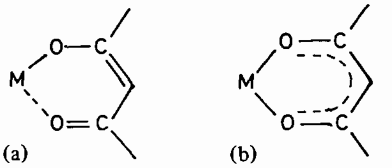

Fig. 1. Coordination modes proposed for (a) $M(mesalen)Ca(bhppH_2)_2$, $M(mesalen)Sr(bhppH_2)$ and $[M(Mesalen)]_2Ba(bhppH_2)_2$, and (b) $M(mesalen)Li(bhppH_2)$ and $M(mesalen)Mg(bhppH_2)_2$ at the metal–β-diketone moiety.

Regarding the nature of the M–O(β-diketone) bond in $M(mesalen)Ca(bhppH_2)_2$, $M(mesalen)Sr(bhppH_2)_2$ and $[M(mesalen)]_2Ba(bhppH_2)_2$ (M = Cu, Ni), a solution similar to those indicated for $M(bhppH_2)_2 \cdot xH_2O$ (M = Ca, Sr, Ba) is proposed [4]. It is due, again, to the IR similarity between both types of compounds in the β-diketone region. The proposed bond consists of a dissymmetric type of metal–β-diketone bond, such as that depicted in Fig. 1a, contrarily to that depicted in Fig. 1b, which is a symmetric one, and expected in $M(mesalen)Li(bhppH_2)$ and $M(mesalen)Mg(bhppH_2)_2$.

References

1 (a) K. Burger, F. Gaizert, M. Pekli, G. Takacsi Nagy and J. Siemroth, *Inorg. Chim. Acta, 92,* 173 (1984); (b) T. Oie, G. H. Loew, S. K. Burt and R. D. MacElroy, *J. Am. Chem. Soc., 106,* 8007 (1984); (c) M. M. Probst and B. M. Rode, *Inorg. Chim. Acta, 92,* 75 (1984); (d) E. Scherer, H A. Tajmir-Riahi and T. Theophanides, *Inorg. Chim. Acta, 92,* 285 (1984); (e) C. V. Prasat and G. R. Pack, *J. Am. Chem. Soc., 106,* 8079 (1984).

2 (a) S. Blanchard and A. M. Tistchenko, *Canad. J. Chem., 62,* 141 (1984) (b) W. O. Lin, M. C. B. V. de Souza and H. G. Alt, *Z. Naturforsch., Teil B, 39,* 1375 (1984).

3 F. Teixidor, A. Llobet, J. Casabó, X Solans, M. Font-Altaba and M. Agulló, *Inorg. Chem., 24,* 2315 (1985).

4 F. Teixidor, T. Flor and J. Casabó, *Inorg. Chim. Acta, 118,* 125 (1986).

5 F. Teixidor, T. Flor, J. Casabó, C. Miravitlles, J. Rius and E. Molins, *Inorg. Chim. Acta, 122,* 95 (1986).

6 F. Eiden and H. D. Schweizer, *Synthesis,* 511 (1974).

7 C. J. O'Connor, D. P. Freyley and E. Sinn, *Inorg. Chem., 18,* 1077 (1979).

8 J. A. Kanters, W. J. J. Smeets, A. J. M. Duisenberg, K. Venkatasubramanian and N. S. Poonia, *Acta Crystallogr., Sect. C, 40,* 1699 (1984).

9 J. A. Kanters, W. J. J. Smeets, K. Venkatasubramanian and N. S. Poonia, *Acta Crystallogr., Sect. C, 40,* 1701 (1984).

10 (a) Z. Y Du, *Acta Crystallogr., Sect. B, 38,* 3095 (1982); (b) M. A. Pierce-Butler, *Acta Crystallogr., Sect. B, 38,* 3100 (1982).

11 R. Stanfield, S. R. Ernst, M. L. Hackert, V. Vijaywargia, K. Venkatasubramanian and N. S. Poonia, *Acta Crystallogr., Sect. C, 40,* 1681 (1984).

12 M. I. Bruce, J. K. Walton, B. W. Skelton and A. H. White, *J. Chem. Soc., Dalton Trans.,* 2221 (1982).