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INTERACTIONS OF HEXAMETHYLTETRABUTYL-SUBSTITUTED BILADIENE-*a,c* WITH COBALT(II) AND ZINC(II) ACETATES

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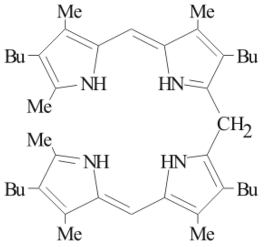
The thermodynamics of the reaction of 1,3,7,13,17,19-hexamethyl-2,8,12,18-tetrabutylbiladiene-*a,c* (H_2L) with cobalt(II) and zinc(II) acetates in dimethylformamide (298.15 K) was studied by spectrophotometric and calorimetric titration. It was found that H_2L and Zn(II) form a mononuclear complex ZnL, and in the case of Co(II), a binuclear biligand complex Co_2L_2 is formed. Thermodynamic characteristics of the formation of Co(II) and Zn(II) complexes with biladiene-*a,c* in DMF at 298.15 K were determined.

Keywords: *biladiene-a,c, binuclear biligand complex, calorimetric titration, mononuclear complex, spectrophotometric titration*

Introduction

According to the current views [1–5], linear tetrapyrroles are capable of selective complexation with *d*-metal ions and various low-molecular-mass ligands. In order to study the chelating behavior of biladiene-*a,c* towards *d*-metal ions and the composition as well as the thermodynamic stability of the resulting chelates, the complexation of 1,3,7,13,17,19-hexamethyl-2,8,12,18-tetrabutylbiladiene-*a,c* (H_2L) with Co(II) and Zn(II) acetates, used conventionally in the preparative synthesis of porphyrins and phthalocyanines [1, 5], was investigated by spectrophotometric and calorimetric titration [4].



Scheme 1

Dimethylformamide, which exhibits satisfactory solvating properties with respect to both the reactants and reaction products, was chosen as the medium.

Experimental

Materials and methods

The compound H_2L was prepared by deprotonation of dihydrobromide $H_2L\cdot 2HBr$ synthesized by a reported procedure [6]. The UV/Vis spectra of the ligand H_2L and the salt $H_2L\cdot 2HBr$ in organic solvents were in agreement with published data [7].

Chemically pure grade DMF was additionally purified by standard procedures [8]. The water content determined by amperometric titration by the Fischer method did not exceed 0.02%. The reactions in the systems were investigated by spectrophotometric and calorimetric titration at 298.15 K. The UV/Vis spectra were recorded on a Specord M40 spectrophotometer in a thermostated cell (the temperature was kept within 0.1 K). Calorimetric measurements were performed on a precision calorimeter with a variable-temperature isothermal shell at 298.15 K.

The composition, the equilibrium concentrations, and the apparent molar absorption coefficients of metal complexes were determined by the method of molar ratios [9, 10]. The reactant concentrations were varied from 10^{-6} to 10^{-4} mol L^{-1}.

Results and discussion

Oligopyrrole hydrobromides containing the chelating ligand in the protonated form are usually used in the template synthesis of tetraaza macrocycles. The protonated ligands are known [11] to be, most often, much less reactive than the free base. To study the thermodynamics of complexation of *d*-metal salts with linear oligopyrroles the electron-donating DMF has been chosen. The reactivity of the chelating ligand can be markedly increased by increasing the amount of nucleophilic components, in particular, DMF, in the reaction mixture [11]. In addition, DMF has an optimal combination of the dielectric permeability (ε^{298}= 36.71), electron-donating properties (*DN*=26.6), and the degree of association, which ensure higher solu-

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bility of low-polarity chemical forms of the reactants and reaction products (or such as oligopyrrole ligands, their complexes, and *d*-metal salts) with organic acids [11]. Data on the solubility and the state of copper and cobalt acetates in DMF were reported [11]. The increase in the solubility of $M(AcO)_2$ in DMF with respect to that in nonpolar solvents was shown to be due to the additional coordination of the molecular electron-donating ligands by the complex-forming metal atom with formation complexes like $[M(AcO)(Solv)_4](AcO)$. In solvents with relatively high dielectric constants, the outer-sphere solvation complexes are capable of primary electrolytic dissociation. As a consequence, the following equilibria are established in solutions of *d*-metal acetates in DMF:

$$[M(AcO)_2(DMF)_4]+DMF \Leftrightarrow [M(AcO)(DMF)_5](AcO)$$

$$[M(AcO)(DMF)_5](AcO) \Leftrightarrow [M(AcO)(DMF)_4]^+AcO^-$$

The solubility study of *d*-metal acetates together with kinetic characteristics of the tetraphenylporphyrinates formation demonstrated that solvated cations are much more reactive than the neutral solvation complexes [11].

The complexation of Zn(II) and Co(II) acetates with H_2L is accompanied by a pronounced change in the intensity. A bathochromic shift (71–77 nm) of the long-wavelength absorption band in the UV/Vis spectra of the complex with respect to the free ligand is also observed (Fig. 1a, b). These differences in the positions of the characteristic absorption bands allowed the use of spectrophotometric methods of molar ratios and isomolar series being used to determine the equilibrium concentrations of the chromophoric reactants and reaction products, the stoichiometric composition of the resulting complexes, and the concentration complexation constants. The UV/Vis spectra of solutions with c_{H2L}=const. and variable concentrations of the salt exhibit a family of isosbestic points, indicating the existence of two colored species in the solution. In both systems, the molar ratio diagram curves show the only intersection point for a 1:1 molar ratio at c_{H2L}=const. and c_{salt}=const. (Fig. 2a, b).

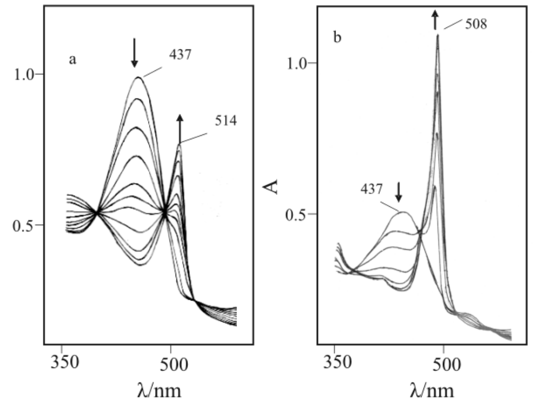


Fig. 1 Variation of the UV/Vis spectra in the a – H_2L–$Co(AcO)_2$–DMF and b – H_2L–$Zn(AcO)_2$–DMF systems at a constant c_{H2L} equal to a – $2.04\cdot10^{-5}$ and b – $1.61\cdot10^{-5}$ mol L^{-1}

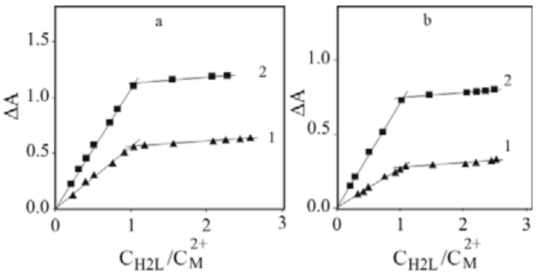
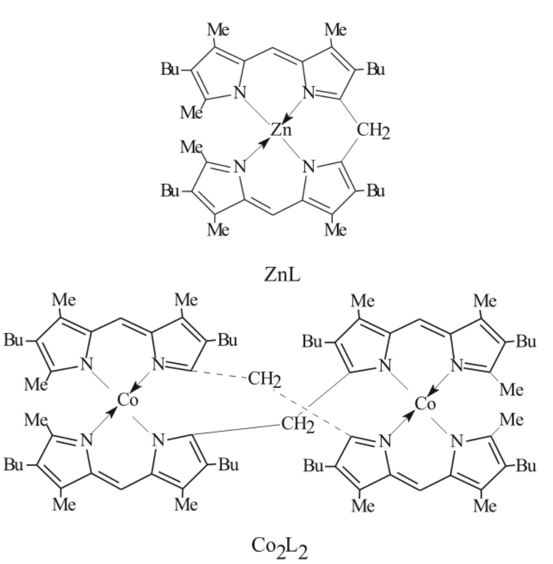


Fig. 2 Curves of molar ratios for the 1 – H_2L–$Co(AcO)_2$–DMF and 2 – H_2L–$Zn(AcO)_2$–DMF systems a – at a constant salt concentration: $c^o_{Co(AcO)_2}=1.81\cdot10^{-5}$, $c^o_{Zn(AcO)_2}=1.79\cdot10^{-5}$ mol L^{-1}; and b – at a constant ligand concentration: 1 – $c^o_{H_2L}=1.35\cdot10^{-5}$ and 2 – $1.44\cdot10^{-5}$ mol L^{-1}

Due to the auxochrome effect of the metal atom on the chromophore π-system at a nearly 100% degree of conversion of the metal ion or the ligand, the complex formation with Zn^{2+} is accompanied by an almost twofold increase in the intensity of the characteristic band in the UV/Vis spectrum of the solution. The system involving $Co(AcO)_2$ showed an opposite behavior, which may be explained by the decrease in the concentration of chromophore species upon binding of two biladiene ligands in one complex molecule.

The elucidated features provide the following conclusions:

- a porphyrin-like complex ZnL is formed in the H_2L–$Zn(AcO)_2$–DMF system;
- a Co_2L_2 complex with a doubly interlaced structure is formed in the H_2L–$Co(AcO)_2$–DMF system [12–14]:



Scheme 2

Table 1 Complexation of zinc and cobalt with biladiene-*a,c* (H_2L), equations for the calculation of the concentration (K_c) and standard equilibrium constants (K^o)*

Reaction scheme	$H_2L+[ZnAcO]^+ + AcO^- \Leftrightarrow$ $ZnL+2AcOH$	$2H_2L+2[CoAcO]^+ +2AcO^- \Leftrightarrow$ $Co_2L_2+4AcOH$
Equations for the calculation of the concentration constant K_c	$K_c=\frac{[ML][HAcO]^2}{[MAcO^+][AcO^-][H_2L]}$	$K_c=\frac{[M_2L_2][HAcO]^4}{[MAcO^+]^2[AcO^-]^2[H_2L]^2}$
$\lg K_c=\lg K^o - a\,c^{1/2}$	$\lg K_c=5.67-951.88c^{1/2}$ $R^2=0.9806$	$\lg K_c=12.55-1131.61c^{1/2}$ $R^2=0.9718$

*The equilibrium concentrations of ZnL and Co_2L_2 complexes were determined using lgε=4.832 (at 508 nm) and 4.609 (at 514 nm), respectively, obtained from spectrophotometric data

The results obtained and the data on the state of *d*-metal acetates in electron-donating DMF suggest that the formation of the ZnL complex is accompanied by replacement of AcO^- and partial displacement of molecular ligands from the inner coordination sphere of the complex cation, $[Zn(AcO)(DMF)_5]^+$, as well as the formation of Zn–L coordination bonds. The Co_2L_2 complex may have been formed through the intermediate formation of unstable $Co_2L(AcO)_2$ complex.

The characteristic types of the complexation of zinc and cobalt acetates with H_2L, the corresponding equations for the concentration equilibrium constant (K_c), and the correlation dependences of $\lg K_c$ on the initial salt concentration are presented in Table 1. The equilibrium constants determined at different concentrations of the initial salt were normalized with the assumption that the solvation complexes $[M(AcO)(DMF)_5]^+(AcO)^-$ completely dissociate in the dilute solutions used. The activity coefficients of non-electrolytes (the ligand and metal complexes) and acetic acid (for which p*Ka* in DMF is 13.3 [15]) were taken to be unity. In view of the low ionic strength of the medium ($I<0.1$) created by dissociation of the solvation complexes, the variation of the concentration equilibrium constants was described by the equation calculating of the average activity coefficient of an electrolyte in terms of the first Debye–Huckel approximation [16, 17]:

$$\lg K_c=\lg K^o - a\,c^{1/2}$$

where $\lg K_c$ and $\lg K^o$ are the logarithms of the concentration and standard complexation constants, respectively; *a* is the coefficient taking into account the solvent polarity, the temperature, etc.; and *c* is the metal acetate concentration (mol L^{-1}) (Table 1).

Calorimetric titration was used to describe the whole thermodynamic picture of the complexation processes in the systems under study. The experimental details have been reported previously [3]. The heat of complexation (ΔQ) [18] was found as the difference between the heats of dissolution of the biladiene ligand in a salt solution (ΔQ_2) and in the pure solvent (ΔQ_1), i.e.

$$\Delta Q=\Delta Q_2-\Delta Q_1$$

The curves for variation of ΔQ *vs.* the c_{H2L}/c_M^{2+} ratio at a constant salt concentration for the H_2L–$M(AcO)_2$–DMF systems (*M*=Zn, Co) exhibit one clear-cut kink at 1:1 molar ratio of the reactants (Fig. 3). This confirms the results obtained by the molar ratio method. At a large excess of the ligand,

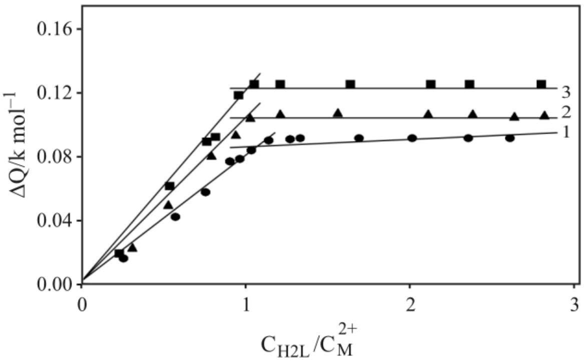


Fig. 3 Calorimetric titration curves for the 1 – H_2L–$Zn(AcO)_2$–DMF and 2, 3 – H_2L–$Co(AcO)_2$–DMF systems at a constant salt concentration: 1 – $c^o_{Zn(AcO)_2}=3.2\cdot10^{-5}$, 2 – $c^o_{Co(AcO)_2}=1.83\cdot10^{-5}$, 3 – $2.14\cdot10^{-5}$ mol L^{-1}

Table 2 Thermodynamic characteristics of the formation of Co(II) and Zn(II) complexes with biladiene-*a,c* in DMF at 298.15 K

Compound	$K^{\circ}(\lg K^{\circ})$	$-\Delta G^{\circ}$/kJ mol^{-1}	$-\Delta H^{\circ}$/kJ mol^{-1}	$-\Delta S^{\circ}$/kJ mol^{-1} K^{-1}
Co_2L_2	$3.58\cdot10^{12}$ (12.55) $R^2=0.9718$	71.7±2.1	196.8±4.4	420±28
ZnL	$4.68\cdot10^5$ (5.68) $R^2=0.9806$	32.4 ± 1.1	38.2 ± 0.5	20 ± 1

the ΔQ value changes slightly. The thermodynamic characteristics of the complexes formation were calculated using the findings obtained for reactant concentration ratios $c_{H2L}:c_{M^{2+}}\geq 1$, which corresponds to the highest product yield. The results of the experiments carried out at different initial concentrations of the salt, show that the enthalpy characteristics of the processes do not depend on the reactant concentrations. The standard enthalpies (ΔH^o), free energies (ΔG^o), and entropies (ΔS^o) of the formation of Co(II) and Zn(II) complexes with biladiene-*a,c* are presented in Table 2.

The high negative values of ΔS^o and ΔH^o for the process of formation of the Co_2L_2 complex are caused by effective binding of two ligands by two Co^{2+} ions within the same coordination species. The formation of the mononuclear ZnL is accompanied by almost twice smaller negative ΔG^o changes and other thermodynamic characteristics. The formation of the porphyrin-like structure of the biladiene complex is more favorable in the terms of entropy standpoint.

To summarize the data on the thermodynamics and formation conditions of transition metal complexes with biladiene-*a,c*, some practical conclusions can be drawn.

Conclusions

- Zinc(II) should be used as the template to efficiently bind bidentrate ligands in the template synthesis of porphyrins from alkyl-substituted biladiene-*a,c*, while the formation of M_2L_2 (in the case of Co(II)) decreases the synthesis efficiency [19].
- The differences between the chelating properties of the tetrapyrrole ligand with respect to Co^{2+} and Zn^{2+} ions can be used in analysis, extraction, and separation of metal mixtures in organic solvents.

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