辅酶 B_{12} 模型化合物的研究

Ⅰ.双水杨醛缩乙二亚胺烷基钴(Ⅲ)配合物 Co-C 键的性质

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本工作合成、表征了一系列辅酶 B_{12} 模型化合物 RCo(Salen)L，其中 R = CH_3, C_2H_5, *n* 和 *i*-C_3H_7, *n* 和 *i*-C_4H_9。研究了上述配合物固体和溶液的 Co-C 键稳定性，结果表明：固体配合物 Co-C 键断裂的温度受烷基位阻影响，它们具有以下顺序：$CH_3 > C_2H_5 > n\text{-}C_3H_7 \approx n\text{-}C_4H_9 \approx i\text{-}C_4H_9 \approx i\text{-}C_3H_7$。此外还确定了影响配合物 Co-C 键在溶液中稳定性的因素。

关键词： 烷基钴配合物 Co-C 键 双水杨醛缩乙二亚胺 辅酶 B_{12}

STUDY ON COENZYME B12 MODEL COMPOUNDS

Ⅰ.THE PROPERTIES OF COBALT-CARBON BOND OF ALKYL COBALT (Ⅲ) COMPLEXES OF BIS (SALICYLALDEHYDE) ETHYLENEDIIMINE

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A series of RCo(salen)L (R = CH_3, C_2H_5, *n* and *i*-C_3H_7, *n* and *i*-C_4H_9) were synthesized and characterized. The stabilities of Co-C bond of title complexes in solid state and in solution was studied. The obtained results showed that the cleavage temperature of Co-C bond of complexes in solid state was effected by the steric bulk of alkyl groups in the following order: $CH_3 > C_2H_5 > n\text{-}C_3H_7 \approx n\text{-}C_4H_9 \approx i\text{-}C_4H_9 \approx i\text{-}C_3H_7$. The factors that influenced the stabilities of Co-C bond of complexes in solution were ascertained.

Keywords: alkyl cobalt complex cobalt-carbon bond
bis(salicylaldehyde) ethylenediimine coenzyme B_{12}

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Introduction

As well known, coenzyme B12 (5′-deoxyadenosylcobalamin) was the first example of a naturally occuring organometallic compound. It serves as a cofactor for various rearrangement reactions in biological systems. Its role can be described as a "reversible free radical carrier"[1]. It is now widely accepted that coenzyme B12-dependent rearrangements are initiated by enzyme-induced homolitic dissociation of the cobalt-carbon bond to generate a 5′-deoxyadenosyl radical. Accordingly, a knowledge of the Co-C bond dissociation energy are useful to explain the mechanism of the coenzyme B12 dependent rearrangements. It is also important to prepare the related organocobalt compounds containing Co-C bond as the coenzyme B12 model and to study the physical and chemical properties of them. This paper reports studies on a series of coenzyme B12 model compounds-alkylcobalt complexes of bis(salicylaldehyde)ethylenediimine [RCo(salen)L], including their properties of Co-C bond and the factors that influence the dissociation of Co-C bond.

Experimental

1. Starting Materials

$CoCl_2 \cdot 6H_2O$, $NaBH_4$, $PdCl_2$, CH_3I, C_2H_5Br were A.R. grade. Other reagents were C.P. grade.

Methanol, salicylaldehyde and alkalkyl halide were purified by distillation.

2. Apparatus and Methods

Elemental analysis of C,H,N(%) were determined using a 240C-elemental analysis instrument. PAR[4 (2 pyridylazo) resorcinol)] colorimetry at 536 nm on 721 spectrophotometer was adopted to determine Co(%) in RCo(salen)L [2].

Infrared spectra were recorded on a Shimadzu IR-400 spectrophotometer with KBr pellets.

UV-visible spectra were obtained using a Shimadzu UV-240 spectrophotometer under nitrogen in the dark.

Thermogravity(TG) and differential scanning calorimetry(DSC) were performed at Perkin Elmer 7 series thermal analysis system under nitrogen flow 40 ml / min and temperature increasing rate 10℃ / min.

3. Preparation of RCo(salen)L

Generally, RCo(salen)L were prepared by the procedure of Schrauzer [3]. Co,C,H,N(%) of above organometallic derivatives were reported in Table 1.

Table 1 Analysis of RCo(salen)L Complexes

complexes	C%		H%		N%		Co%	
	calcd.	found.	calcd.	found	calcd.	found	calcd.	found.
$CH_3Co(salen) \cdot H_2O$	56.98	56.55	5.35	5.17	7.82	7.86	16.45	16.58
$C_2H_5Co(salen)$	61.01	61.12	5.40	5.47	7.90	7.73	16.63	16.72
n-$C_3H_7Co(salen) \cdot H_2O$	59.07	58.90	6.00	5.97	7.25	7.31	15.25	15.25
i-$C_3H_7Co(salen)$	61.92	61.59	5.70	6.01	7.60	6.95	16.00	16.07
n-$C_4H_9Co(salen) \cdot H_2O$	59.99	60.44	6.28	6.24	6.99	6.61	14.72	14.72
i-$C_4H_9Co(salen) \cdot H_2O$	59.99	59.71	6.28	5.80	6.99	7.04	14.72	14.70

Results and Discussion

Among obtained six complexes the i–C_4H_9 derivatives is firstly reported. According to element analysis the formular of the complexes are RCo(salen) · H_2O when R = CH_3, *n*–C_3H_7, *n*–C_4H_9 and *i*–C_4H_9. But there is the absence of water for R = C_2H_5 and *i*–C_3H_7. These two complexes were different from Schrauzer's [3] but same as Costa's [4] who prepared RCo(salen)L using Grinard reagent in THF. Futhermore, the IR, TG and DSC experiments give additional evidence about the existence of coordinated water in those organocobalt complexes.

Infrared Spectra [5]

The I_R spectra of alkylcobalt(Ⅲ) complexes all show strong C=N vibration at 1625cm^{-1}. The saturated C–H stretching vibration is expected in the range 2800–2950cm^{-1}. Three bands of aromatic C=C vibration of the aromatic ring conjugated to a doubled bond are at 1600–1530cm^{-1}. The asymmetrical vibration of the CH_3 group absorbs at 1450 ± 20cm^{-1}. The inplane vibration of the CH= occurs between 1450 and 1200cm^{-1}. The band at 1340cm^{-1} shows the vibration of C–O after chelating. The strong absorbance between 750–760cm^{-1} are deformation vibration of C–H band in benzen ring plane. The vibration frequency of Co–O and Co–N are expected between 300–500cm^{-1}. The vibration frequency of Co–C is in this range too.

The broad absorption band around 3200–3400cm^{-1} shows the symmetric stretching vibration of OH–group in methyl, *n*–propyl, *n*–butyl and *i*–butyl derivatives. But for ethyl and *i*–propyl cobalt(Ⅲ) complex, no water peak appears at 3200–3400cm^{-1}. The bent vibration of OH–over the range at 1615–1645cm^{-1} was suppressed by the strong C=N vibration.

Cleavage of Co–C Bond in Solid

The complexes are stable at room temperature. Their melting point cannot be determined. When heated the complexes change their colour and lose their weight.

TG and DSC data of alkylorganometallic derivatives are summarized in Table 2. The TG and DSC curves of n–butyl and ethyl derivatives are shown in Fig.1 and Fig.2.

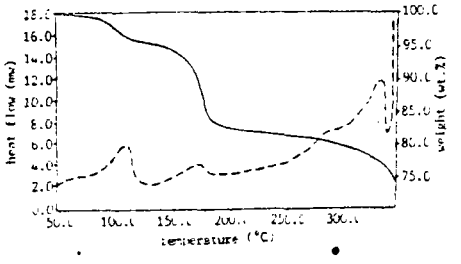

Fig.1 TG(—) and DSC(——) curve of *n*–C_4H_9Co(salen) · H_2O

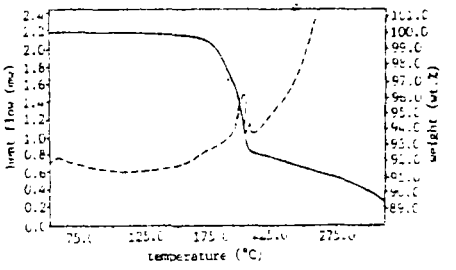

Fig.2 TG(—) and DSC(——) curve of C_2H_5Co(salen)

Table 2 TG and DSC Data of Complexes

complexes	mol. weight	temperature range(℃)	losing weight (%)		changing substance	DSCpeak (℃)
			calcd.	found		
$CH_3Co(salen)\cdot H_2O$	358.27	53~131	5.02	5.06	$-H_2O$	120
		133~226	4.19	4.00	$-CH_3$	224
$C_2H_5Co(salen)$	354.28	141~210	8.19	7.43	$-C_2H_5$	201
$n-C_3H_7Co(salen)\cdot H_2O$	386.22	47~126	4.66	3.60	$-H_2O$	97
		126~196*	11.13	10.57	$-C_3H_7$	158,182
$i-C_3H_7Co(salen)$	368.20	45~262	12.25	11.74	$-C_3H_7$	158
$n-C_4H_9Co(salen)\cdot H_2O$	400.35	54~124	4.50	4.18	$-H_2O$	105
		124~247	14.27	14.50	$-C_4H_9$	170
$i-C_4H_9Co(salen)\cdot H_2O$	400.35	57~132	4.50	4.30	$-H_2O$	104
		132~350	14.27	14.80	$-C_4H_9$	165

* there are two minimum at 150℃ and 182℃ on derivative TG curve which are corresponding to the two endo peaks

It can be seen that the thermolysis process of methyl, *n*-propyl, *n*-butyl complexes between 40℃ and 350℃ was divided into two stages: the dehydration around 100℃ indicating containing coordinate water and then the cleavage of cobalt-carbon bond at higher temperature. But only one step for ethyl and *i*-propyl cobalt derivatives, which refers to the cleavage of Co-C bond. This results in the same conclusion as from IR spectra that no coordinate or crystal water in ethyl and *i*-propyl cobalt complexes.

From Table 2, the cleavage temperature of Co-C bond decreases with changes of R in the following order: $CH_3 > C_2H_5 > n-C_3H_7 \approx n-C_4H_9$. While the alkyl group are isomer, the cleavage temperature decreases with the increasing of steric bulk of R. For instance, the cleavage temperature of $i-C_4H_9Co(salen)\cdot H_2O$(165℃)is lower than that of $n-C_4H_9Co(salen)\cdot H_2O$(170℃). Accordingly, the results show that the cleavage of cobalt-carbon bond was effected by the steric bulk of axial alkyl ligand.

It is worth noticing that on DSC curve of $CH_3Co(salen)\cdot H_2O$ the cleavage of Co-C bond was a exothermic process, while for other RCo(salen)L complexes that were endothermic. It appears that the alkyl radicals formed by thermolysis underwent futher reaction. The products will be detected by GC and the mechanism will be discussed later.

UV-visible Spectrometry

The UV-visible spectra of complexes in methanol and methylene chloride are determined. In methylene chloride all the derivatives give one shoulder at about 390nm. In Table 3 are listed the wavelengths of the absorption maxima found in the visible and ultra-violet regions where the abbreviation sh indicate the band is weak and occurs as a shoulder. The corresponding approximate molar extinction coefficients (lg ε) are enclosed in parenthese.

Table 3　UV-visible Spectra Data of Complexes

R	λmax, nm (lgε)			
CH_3	330(3.84)	385sh(3.68)	437sh(3.40)	520sh(3.04)
C_2H_5	332(3.99)	385sh(3.77)	454sh(3.44)	540sh(3.04)
n-C_3H_7	328(3.80)	390sh(3.62)	450sh(3.29)	520sh(2.89)
i-C_3H_7	332(3.97)	390sh(3.72)	450sh(3.28)	
n-C_4H_9	332(3.79)	390sh(3.57)	452sh(3.10)	540sh(2.86)
i-C_4H_9	335(3.94)	390sh(3.68)	460sh(3.29)	540sh(2.92)

The electronic spectra of the organocobalt(Ⅲ) complexes are usually complicated and difficult to be assigned. In the electronic spectra of RCo(salen)L, the intense band at 330–340nm can be ascribed to a charge transfer absorption involving metal ion and ligand. While the shoulders in the region 400–600nm are probably due to d–d transition [6].

Cleavage of Co–C Bond in Solution

At room temperature, the UV-visible spectra of alkylcobalt complexes in methonal were changed with time, the changing rate of i-propyl cobalt(Ⅲ) complex is most rapid. We investigated in following experiments to elucidate the reason and to find the products of those changes. The results were given in Fig.3 for $CH_3Co(salen) \cdot H_2O$.

(1) In the light without nitrogen, the spectra changed in half an hour. The intensity of the peak at 325nm decreased while a shoulder appeared around 388nm and growed to a peak in three hours (Fig.3a).

(2) Under nitrogen in the dark, and intensive absorption at 330nm was given. The intensity didn't change for hours.(Fig.3b, curve 1–5).

(3) Under nitrogen in the light, a new absorption at 388nm appeared with time while the peak at 330nm disappeared.(Fig.3b, curve 6–7).

It can be seen that at room temperature light is the main factor that influence the stability of RCo(salen)L solutions. to ascertain this, the methanol solution of alkylcobalt(salen) was irradiated by the UV-lamp or heliolamp for an hour. The final absorption appeared at 388nm with the same intensity as that of a methanol solution of Co(salen)L in same concentration.

Futhermore, similar absorption changes of the RCo(salen)L solution with time happened at 50℃ as illustrated by Fig.4. The absorbances changed with time. The intensities of the bands around 330nm decreased while shoulders at 388nm growed to be a peak. It is worth of attention that the final spectrum, which is the same as that of Co(salen)L, also can be got by irradiation the initial solution on UV-lamp.

Above results show that the solutions of RCo(salen)L result in the cleavage of Co–C bond when heated or irradiated by light. Products from those proceess include Co(salen)L. The reaction is expected as following:

$$RCo(salen)L \xrightarrow[heat]{h\nu \text{ or}} Co(salen)L + R\cdot$$

The existence of R · has been determined by ESR. The details are to be reported.

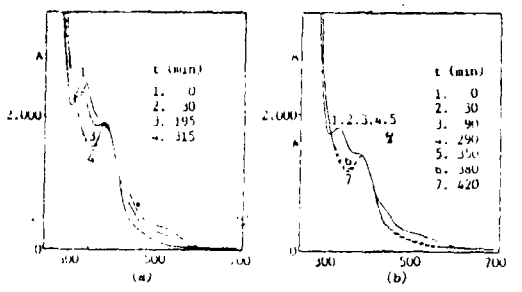

Fig.3 Changes in absorbance with time of $CH_3Co(salen) \cdot H_2O$ in methanol at room temperature
(a) without N_2, in the light, 3.84×10^{-4} mol • l^{-1}
(b) under N_2, in the dark(—); under N_2, in the light(——), 3.00×10^{-4} mol • l^{-1}

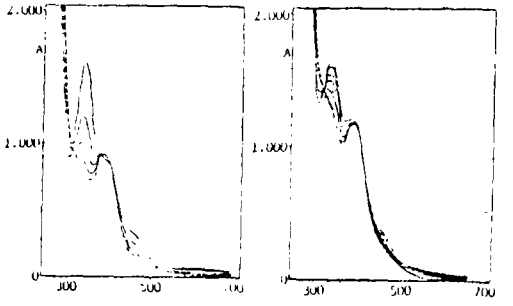

Fig.4 Changes in absorbance with time of butylcobalt (salen)L in methanol at 50℃, time interval 30 min.
—— final absorbance of solutions which had been exposed to light for 1.0 hour
(a) i–C_4H_9 Co(salen) • H_2O
3.0×10 mol • l^{-1}
(b) n–C_4H_9 Co(salen) • H_2O
2.6×10^{-4} mol • l^{-1}

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