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STUDIES ON THERMAL STABILITY AND KNOT FORMATION IN THE TG CURVES OF Co(III) MODEL COMPLEXES

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TG studies of vitamin B_{12} coenzyme model complexes, BrCo(diacetylmonoximeiminatodiacetylmonoximatoiminobenzene-1,6)L have been carried out with different heating rates and sample sizes. The trans ligand, L, is bromine, imidazole, methylimidazole, pyridine or triphenylphosphine. The decompositions of the complexes (except for the triphenylphosphine complex) are associated with the formation of a knot at the point of completion of the inflection of the TG curve at a heating rate of 20 deg/min; such a phenomenon is not observed for rates of 10 and 5 deg/min. The formation of a knot with increase in weight and decrease in temperature is attributed to the transition from high-energy six-coordinate Co(III) species to low-energy five-coordinate Co(II) species. The triphenylphosphine complex is found to deviate from these characteristics of decomposition.

The roles of the coenzymes of vitamins in enzymatic reactions have gradually been revealed in recent years. The fundamental roles of the vitamins in the metabolic process are not limited to the haemopoietic system, but occur throughout the body [1, 2]. Much of the vitamin B_{12} in the organism seems to exist in coenzyme form. 5'-Deoxyadenosylcobalamin has been isolated as the coenzyme of vitamin B_{12} from *Clostridium tetanomorphum* [3]. All coenzymes contain cobalt, which lies approximately in the plane of the four nitrogens of the corrin ligand. The features of this macrocyclic ligand as concerns the binding to the protein are not yet clearly understood. The chemical or structural features which are important in directly or indirectly influencing the course of the enzymatic reaction have not yet been explored thoroughly either. Model complexes have been developed with varying macrocyclic ligand and axial ligand, to isolate or represent particular features of coenzyme B_{12}, making the latter more amenable to experimental or theoretical

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investigation [4–12]. However, the characterization of coenzyme B_{12} and the variation in thermal stability of these model complexes stimulated the search for a better model and studies on the effect of the thermal environment on their stability. The present work deals with TG studies on cobalt(III) planar equatorial macrocyclic ligand complexes of formula RCo(chelate)L.

Experimental

The macrocyclic ligand used for the present studies was diacetylmonoximeiminatodiacetylmonoximatoiminobenzene-1,6 [(DO)(DOH)bz] with bromine as one axial ligand. The trans ligand was varied as mentioned in Table 1.

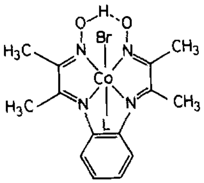

Table 1 Vitamin B_{12} coenzyme model complexes

No.	Trans ligand	Complex	Nature of complex
1	Br	BrCo[(DO)(DOH)bz]Br	neutral
2	imidazole	BrCo[(DO)(DOH)bz]-imidazole	1 : 1 electrolyte, counter-anion BF_4
3	methyl-imidazole	BrCo[(DO)(DOH)bz]-methylimidazole	1 : 1 electrolyte, counter-anion BF_4
4	pyridine	BrCo[(DO)(DOH)bz]-pyridine	1 : 1 electrolyte, counter-anion BF_4
5	triphenyl-phosphine	BrCo[(DO)(DOH)bz]-triphenylphosphine	1 : 1 electrolyte, counter-anion PF_6

A Dupont 951 TGA coupled with a 990 Thermal Analyser was used. The heating rate was 5, 10 or 20 deg/min. The analyses were carried out in air from ambient up to 400°. Samples ranging from 5 mg to 15 mg were taken in a platinum sample holder. The temperatures were recorded using a chromel-alumel sample thermocouple. Two runs were generally taken for each sample to confirm the values of temperature, weight loss and activation energy.

Results and discussion

Corrin-type ligands exhibit relatively low variations in their properties when the planar ligand is varied [9–12]. However, different axial ligands have different bond lengths with the cobalt, which gives rise to considerable differences in the properties. The changes in the properties of the present model complexes were increased further by varying both the axial and the trans ligand, as is observed from the thermal stabilities. The peak temperature (*TS*) of the thermogravimetric curve at a heating rate of 20 deg/min and a sample size of 5 mg (Tables 2–6) follow the sequence:

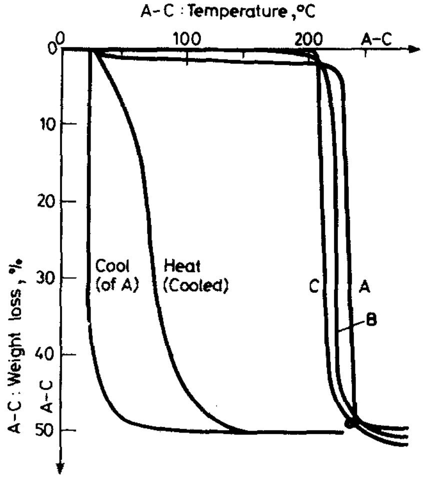

Fig. 1 TG curves of BrCo[(DO)(DOH)bz]Br. Sample size 5 mg. (A: heating rate 20 deg/min, B: 10 deg/min, C: 5 deg/min)

BrCo[(DO)(DOH)bz]pyridine = BrCo[(DO)(DOH)bz]imidazole >
> BrCo[(DO)(DOH)bz]methylimidazole > BrCo[(DO)(DOH)bz]Br >
> BrCo[(DO)(DOH)bz]triphenylphosphine.

The strong ligand field provided by the [(DO)(DOH)bz] ligand contributes to the kinetic stability of the cobalt-axial bond. The availability of π-orbitals in the planar ligand may accomodate the extra charge placed on the cobalt, leading to the cobalt-axial bond being only slightly polarized. However, the cobalt-bromine bond is considerably polarized due to the influence of the trans ligand. This introduces appreciable changes in the thermal properties. The electron-withdrawing power of bromine in the axial position of the present model complexes is high, which makes

Table 2 Thermogravimetric analysis of BrCo[(DO)(DOH)bz]Br at different heating rates and sample sizes

No.	Heating rate, deg/min	Sample size, mg	Inception temp. (T_i), °C	Peak temp. (T_s), °C	Final temp. (T_f), °C	Weight loss, mg	Activation energy (E^*) kJ mole^{-1}
1	5	5	203	217	256	2.5	225.10
	5	10	203	219	257	5.0	225.52
	5	15	203	220	258	7.5	226.35
2	10	5	202	225	265	2.5	225.94
	10	10	202	228	268	5.0	226.77
	10	15	202	230	269	7.5	227.61
3	20	5	200	235	275	2.5	226.77
	20	10	200	238	280	5.0	227.19
	20	15	201	240	282	7.5	227.61

the cobalt a good Lewis acid. Due to the electron-withdrawing power of bromine, any ligand trans to the axial bromine ligand is strongly bonded. The trans bromine ligand, however, forms a neutral complex. Because of the greater affinity of cobalt for imidazole, the trans imidazole ligand forms a stronger bond with cobalt, leading to the highest peak temperature (*TS*) of decomposition (Table 3, Fig. 2). Though the methyl group in the trans methylimidazole ligand has a +I effect, which also increases the affinity towards cobalt, the peak temperature is less than that for the trans imidazole ligand complex, due to steric hindrance (Table 4, Fig. 3). The trans

Table 3 Thermogravimetric analysis of BrCo[(DO)(DOH)bz]imidazole at different heating rates and sample sizes

No.	Heating rate, deg/min	Sample size mg	Inception temp. (T_i), °C	Peak temp. (T_s), °C	Final temp. (T_f), °C	Weight loss, mg	Activation energy (E^*) kJ mole^{-1}
1	5	5	245	255	290	1.7	271.96
	5	10	245	257	292	3.4	272.80
	5	15	245	260	293	5.1	273.22
2	10	5	245	263	298	1.7	272.80
	10	10	245	265	299	3.4	273.72
	10	15	246	268	300	5.1	274.05
3	20	5	245	275	305	1.7	273.63
	20	10	246	277	307	3.4	274.05
	20	15	246	278	309	5.1	274.47

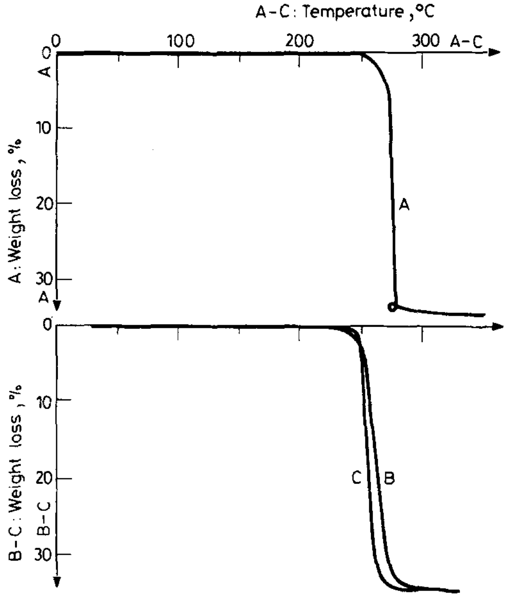

Fig. 2 TG curves of BrCo[(DO)(DOH)bz]imidazole. Sample size 5 mg. (A: 20 deg/min, B: 10 deg/min, C: 5 deg/min)

Table 4 Thermogravimetric analysis of BrCo[(DO)(DOH)bz]methylimidazole at different heating rates and sample sizes

No.	Heating rate, deg/min	Sample size, mg	Inception temp. (T_i) °C	Peak temp. (T_s), °C	Final temp. (T_f), °C	Weight loss, mg	Activation energy (E^*), kJ mole^{-1}
	5	5	207	238	249	0.95	238.91
1	5	10	208	240	251	1.90	239.74
	5	15	208	241	253	2.85	240.58
	10	5	207	246	256	0.95	239.74
2	10	10	208	247	257	1.90	240.16
	10	15	208	249	259	2.85	241.00
	20	5	207	254	265	0.95	240.58
320	20	10	207.5	255	267.5	1.90	241.00
	20	15	208	257	269	2.85	241.42

pyridine ligand also has a high affinity towards cobalt, and the bond breaking of cobalt-pyridine is influenced not only by the bromine ligand but also by the cobalt to nitrogen [of (DO)(DOH)bz] bond strength. Because of the strong cobalt-nitrogen bond in the [(DO)(DOH)bz] ligand, the axial pyridine ligand is strongly

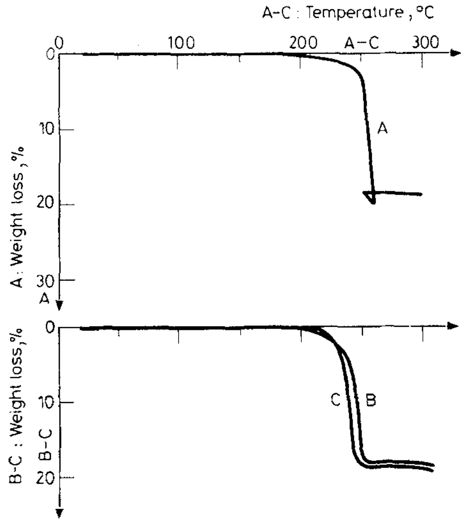

Fig. 3 TG curves of BrCo[(DO)(DOH)bz]methylimidazole. Sample size 10 mg. (A: 20 deg/min, B: 10 deg/min, C: 5 deg/min)

Table 5 Thermogravimetric analysis of BrCo[(DO)(DOH)bz]pyridine at different heating rates and sample sizes

No.	Heating rate, deg/min	Sample size, mg	Inception temp. (T_i), °C	Peak temp. (T_s), °C	Final temp. (T_f), °C	Weight loss, mg	Activation energy (E^*), kJ mole^{-1}
1	5	5	235	258	280	3.05	255.64
	5	10	235	260	281	6.10	256.06
	5	15	235	262	283	9.15	256.90
2	10	5	235	266	290	3.05	256.48
	10	10	235	268	292	6.10	256.06
	10	15	236	271	294	9.15	257.32
3	20	5	235	275	300	3.05	257.32
	20	10	235	277	303	6.10	257.73
	20	15	236	279	305	9.15	258.15

bonded, as exemplified by the highest peak temperature (Table 5, Fig. 4). Moreover, the size of pyridine is more accomodative, with less steric hindrance. Since two bromines are bonded as axial ligands to cobalt in the complex BrCo[(DO)(DOH)bz]Br, the inductive effect is neutral and the cobalt-bromine bond breaking is influenced only by the cobalt-nitrogen bond strength. The trans

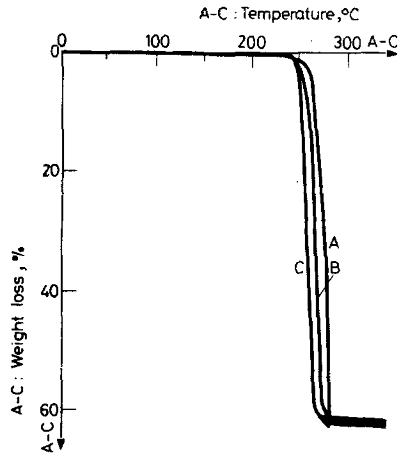

Fig. 4 TG curves of BrCo[(DO)(DOH)bz]pyridine. Sample size 5 mg. (A: 20 deg/min, B: 10 deg/min, C: 5 deg/min)

bromine ligand complex therefore has a low peak temperature (Table 2, Fig. 1). The trans triphenylphosphine ligand complex exhibits the lowest peak temperature, which is due to the high steric hindrance (Table 6, Fig. 5).

The weight loss on decomposition at the peak temperature is more or less proportional to the peak temperature, with an exception in the case of

Table 6 Thermogravimetric analysis of BrCo[(DO)(DOH)bz]triphenylphosphine at different heating rates and sample sizes

No.	Heating rate, deg/min	Sample size, mg	Inception temp. (T_i), °C	Peak (first) temp. (T_s), °C	Final temp. (T_f), °C	Weight loss, mg	Activation energy (E^*), kJ mole^{-1}
1	5	5	212	216	222	0.7	158.57
	5	10	213	217	223	1.4	158.99
	5	15	213	219	225	2.1	159.41
2	10	5	213	220	225	0.7	159.41
	10	10	213	221	226	1.4	159.83
	10	15	214	223	227	2.1	160.25
3	20	5	212.5	225	227	0.7	160.25
	20	10	213	227	230	1.4	160.67
	20	15	213	228	232	2.1	161.08

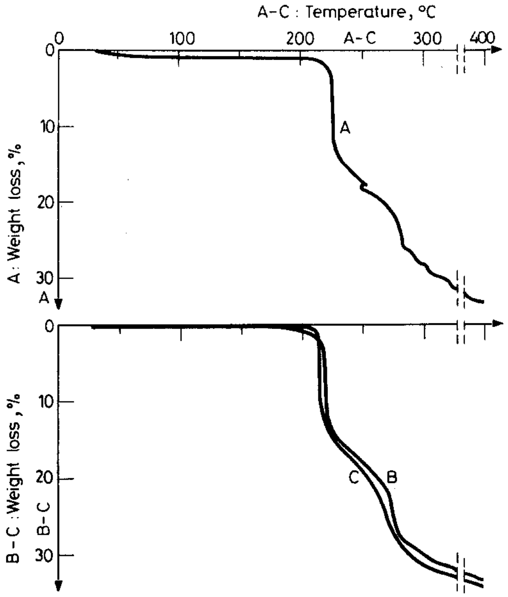

Fig. 5 TG curves of BrCo[(DO)(DOH)bz]triphenylphosphine. Sample size 5 mg. (A: 20 deg/min, B: 10 deg/min, C: 5 deg/min)

BrCo[(DO)(DOH)bz]Br (Tables 2–6). The weight losses of the complexes follow the sequence:

BrCo[(DO)(DOH)bz]pyridine >
BrCo[(DO)(DOH)bz]Br > BrCo[(DO)(DOH)bz]imidazole >
BrCo[(DO)(DOH)bz]methylimidazole >
BrCo[(DO)(DOH)bz]triphenylphosphine.

The higher the peak temperature, the higher the amount undergoing decomposition. The activation energies for the decomposition of the present complexes (Tables 2–6) follow the sequence:

BrCo[(DO)(DOH)bz]imidazole (273.22 ± 1.26 kJ mol^{-1}) >
BrCo[(DO)(DOH)bz]pyridine (256.90 ± 1.26 kJ mol^{-1}) >
BrCo[(DO)(DOH)bz]methylimidazole (240.16 ± 1.26 kJ mol^{-1}) >
BrCo[(DO)(DOH)bz]Br (226.35 ± 1.26 kJ mol^{-1}) >
BrCo[(DO)(DOH)bz]triphenylphosphine (159.83 ± 1.26 kJ mol^{-1}).

The activation energies of the present complexes were calculated via the equation [13]:

$$\ln \ln(1-\alpha)^{-1} = \frac{E^*}{RT_i^2}\frac{100}{(T_f-T_i)}+C$$

Where α = fraction dissociated, E^* = activation energy (cal/mol), R = gas constant (1.987), T_i = temperature of inception of dissociation (K), T_f = temperature of completion of dissociation (K), T_s = temperature at the point of inflection in the TG curve (K), θ = difference between T_s and temperature under consideration $(T-T_s)$, C = constant.

Representative $\ln \ln(1-\alpha)^{-1}$ vs θ plots for the heating rate of 20 deg/min are given in Fig. 6. The above equation was used for the calculation of activation energy, since the transition from six-coordinate species to five-coordinate species (as explained later) may be considered a first-order reaction. The activation energy decreases slowly with decrease in heating rate, and increases with increase in sample size. The latter is attributed to the fact that the activation energy is the amount of energy required per mole of the substance for decomposition.

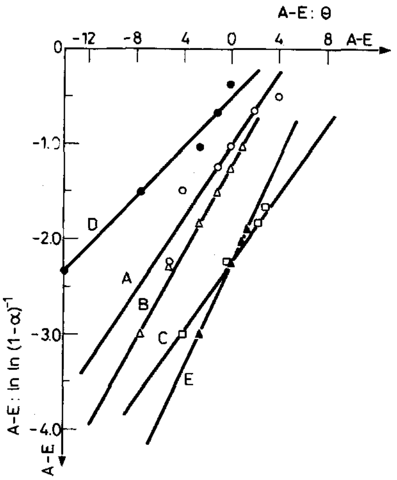

Fig. 6 Typical $\ln \ln(1-\alpha)^{-1}$ vs θ plots at a heating rate of 20 deg/min (A: complex with trans Br ligand, B: imidazole, C: methylimidazole, D: pyridine, E: triphenylphosphine)

Thermogravimetric analysis reveals the variations in peak temperature and final temperature (T_f) with change in heating rate and sample size. Representative TG curves of the complexes for different heating rates with a sample size of 5 mg are given in Figs 1–5. These temperatures increase with increase in sample size and heating rate. However, the temperatures of inception remain almost constant for the decompositions. An interesting feature is observed in the curves for the heating rate of 20 deg/min. All complexes except BrCo[(DO)(DOH)bz]triphenylphosphine exhibit a knot in the completion of the inflection. This knot is not obtained at heating rates of 10 and 5 deg/min (Figs 1–5). The knot is formed by the decrease in temperature (*X* axis) and increase in weight (*Y* axis). This is attributed to the transition from the Co(III) complex to the Co(II) complex during the dissociation.

Under the accelerated heating, the transition from the six-coordinate (Co(III) system to the five-coordinate Co(II) system is made more facile by removing one of the axial ligands. The slow heating facilitates the removal of the axial ligand, which is followed by multiple reduction. The rate of transition from the six-coordinate complex to the five-coordinate complex is very high at a high heating rate, due to the low energy of the five-coordinate complex. The decrease in temperature at the knot is attributed to the transition from the high-energy six-coordinate species to the low-energy five-coordinate species. The Co(III) complex is a low-spin octahedral complex of high symmetry, involving d^2sp^3 hybridization, and is diamagnetic, whereas the Co(II) complex is square pyramidal and paramagnetic, involving d^7. It has been observed that Co(III) corrinoids lack the properties of typical Co(III), especially in the reduction properties [14]. Though Co(III) corrinoids may undergo reduction either in two one-electron steps (Co(III) →(Co(II) →Co(I)) or in one two-electron step (Co(III) →Co(I)), the present model complexes (except for the triphenylphosphine complex) undergo reduction in two one-electron steps at the heating rate of 20 deg/min. This is inferred from the weight gain and the temperature decrease at the knot, which are characteristics of the typical Co(III) →Co(II) transition. Thus, the model complexes behave like ordinary cobalt complexes at the higher rate of heating.

The cooling curves of specimens heated at 20 deg/min and the heating curves of the cooled specimens explain the possible coordination of water in the trans position of the five-coordinate Co(II) species, resulting in distorted octahedral geometry. A representative curve is given by the complex BrCo[(DO)(DOH)bz]Br. The above cooling and heating curves are not exhibited by BrCo[(DO)(DOH)bz]triphenylphosphine and other complexes heated initially at 10 or 5 deg/min. These all confirm the transition Co(III) →Co(II) with weight gain and temperature increase at the knot, for all complexes except BrCo[(DO)(DOH)bz]triphenylphosphine. Moreover, the absence of a knot from the TG curves obtained at the heating rates of 10 and 5 deg/min may be due to the mixed effect of two one-electron steps and one two-electron step of reduction (multiple reduction). The trans triphenylphosphine ligand is easily removed from its complex when the complex is heated at 20 deg/min, due to steric hindrance at low peak temperature. This is followed by faster and uncontrolled decomposition. Accordingly, this complex nature of the decomposition does not yield a knot in the

TG curve. Moreover, the thermal curves obtained at 10 and 5 deg/min represent the same phenomenon (Fig. 5). The formation of the knot is not affected by a change in sample size, as is evident from the curve for BrCo[(DO)(DOH)bz]methylimidazole (Fig. 3). On the other hand, the rate of transition is accelerated by an increase in the sample size.

Conclusion

It has been inferred that decomposition of the present Co(III) model complexes having low steric hindrance proceeds through the transition from the six-coordinate Co(III) system to the five-coordinate Co(II) system only at high heating rate. The transition is demonstrated by a knot in the TG curve, formed on the decrease in temperature (X axis) and the increase in weight (Y axis).

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Zusammenfassung — TG-Untersuchungen von Vitamin-B_{12}-Coenzymkomplexen — BrCo(Diacetylmonoxim-iminato-diacetylmonoximato-iminobenzol-1,6)L wurden bei verschiedenen Aufheizgeschwindigkeiten und mit unterschiedlichen Probenmengen ausgeführt. Der trans-Ligand L ist mit Brom, Imidazol, Methylimidazol, Pyridin bzw. Triphenylphosphin modifiziert. Mit Ausnahme des Triphenylphosphinkomplexes geht die Zersetzung der Komplexe bei einer Aufheizgeschwindigkeit von 20 °/min mit der Ausbildung einer Schleife an der Stelle des TG Kurve einher, an der die Inflektion beendet ist. Solch ein Effekt ist nicht bei Aufheizgeschwindigkeiten von 10 und 5 °/min zu beobachten. Das eten einer Schleife mit zunehmenden Gewicht und abnehmender Temperatur ist der Umwandlung von 6-fach koordinierten Co(III)-Species hoher Energie in 5-fach koordinierte Co(II)-Species niedriger Energie zuzuschreiben. Der Triphenylphosphinkomplex weicht von dieser Zersetzungscharakteristik ab.

Резюме — Для модельных комплексов коэпзима витамина B_{12}, BrCo(диацетил-монооксим-иминато-диацетилмоноксимато-имино-бензол-1,6)L, проведены ТГ исследования при различных скоростях нагрева и размерах образца. В качестве транс-лиганда L были бром, имидазол, метилимидазол, пиридин и трифенилфосфин. Разложение комплексов, за исключением трифенилфосфинового, связано с образованием узла в точке окончания перегиба на термограмме при скорости нагрева 20°/мин. Это явление не наблюдается при скоростях нагрева 10 и 5°/мин. Образование узла с увеличением веса и уменьшении температуры приписано переходу от высокоэнергетических шестикоординационных Co(III) комплексов до низкоэнергетических пятикоординационных (Co(II) комплексов. Найдено, что трифенилфосоновый комплекс отклоняется от этих характеристик разложения.