

Photolytic and thermal properties of a new series of intramolecular bridged alkyl cobaloxime complexes

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The photolytic kinetic properties of a new series of intramolecular bridged alkyl cobaloxime complexes $\text{Br}(\text{O}-\text{C}_3\text{H}_6-(\text{dmgH}))(\text{dmgH})\text{Co}^{\text{III}}$ (**2**), $[\text{H}_2\text{O}(\text{O}-\text{C}_3\text{H}_6-(\text{dmg}))(\text{dmgH}_2)]\text{Co}^{\text{III}}[\text{ClO}_4]$ (**3**), $[\text{Py}(\text{O}-\text{C}_3\text{H}_6-(\text{dmg}))(\text{dmgH}_2)]\text{Co}^{\text{III}}[\text{ClO}_4]$ (**4**), $[\text{Bzm}(\text{O}-\text{C}_3\text{H}_6-(\text{dmg}))(\text{dmgH}_2)]\text{Co}^{\text{III}}[\text{ClO}_4]$ (**5**) and $[\text{Im}(\text{O}-\text{C}_3\text{H}_6-(\text{dmg}))(\text{dmgH}_2)]\text{Co}^{\text{III}}[\text{ClO}_4]$ (**6**) and their precursor aqua-(3-bromopropyl)cobaloximes (**1**) were investigated by UV-Vis spectroscopy. The products of photolytic solutions were characterized by both ESI-MS and ^1H -NMR techniques. Our results revealed a carbon-center radical that is produced from Co–C bond cleavage under photolysis might be linked to the equatorial ligand and thus retained in the proximity of Co^{II} -complex. The thermo-gravimetric analysis of complex **2** gives the same conclusion.

Introduction

Since Schrauzer suggested the method of making alkyl-cobaloximes,^{1,2} a variety of organocobalt(III) complexes with a stable σ Co–C bond have been synthesized and investigated^{3–5} as model complexes for coenzyme B_{12} , *i.e.* 5'-deoxyadenosylcobalamin, which serves as a cofactor for certain enzymatic reactions involving intramolecular 1,2-rearrangements.⁶ Among them intramolecular bridged organocobalt(III) complexes, in which the alkyl ligands link to the equatorial plane, are one type of important coenzyme B_{12} models. The recent X-ray data for methylmalonyl-CoA mutase,^{7,8} glutamate mutase⁹ and diol dehydratase¹⁰ reveal that distances from the Co center of 5'-deoxyadenosylcobalamin to the radical centers on the substrate and product are 6–8 Å in the above three B_{12} enzymes. Further, the former model investigations had provided evidence that in the absence of $\text{Co}(\text{II})$ such a kind of radical did not isomerize.^{11,12} So, the intramolecular bridged organocobalt(III) complexes could mimic the situations of the holo-enzyme where the C-center radical formed from homolysis of the Co–C bond stays in the proximity of a $\text{Co}(\text{II})$ and allows the cobalt intermediate to assist in group migration. In 1980 the first kinds of bridged organocobalt(III) complexes were synthesized and the products of 1,2-rearrangement reaction from photolysis were characterized by Rétey *et al.*^{13,14} However, in the past years only a few of cobaloximes, Cosalen and Costa complexes with bridged structures have been reported.^{15–20}

It is well recognized that the necessary step in the coenzyme B_{12} dependent enzymatic reactions is homolytic cleavage of the Co–C bond, generating a $\text{Co}(\text{II})$ species and a 5'-deoxyadenosyl radical. Like the above enzyme reactions, photolysis or thermolysis of the 5'-adenosylcobalamin and its analogues leads to homolytic cleavage of the Co–C bond.^{21–24} Extended, self-consistent HMO calculations demonstrate a close similarity in the nature of the axial bonds involving the cobalt atom in vitamin B_{12} and in cobaloximes model compounds.²⁵ Therefore, synthesis of the intramolecular bridged organocobalt(III) B_{12} models and investigation of their properties in photolysis and thermolysis are of consequence. Comparison of the properties of these species to those of the non-bridged models might help to understand the role of $\text{Co}(\text{II})$ in B_{12} -catalyzed 1,2-rearrangement. Recently, we have prepared and characterized a new series of intramolecular bridged alkyl cobaloxime complexes.²⁶ In the present work, the photolytic and thermal properties of them are studied by UV-Vis, ESI-MS, ^1H -NMR and TG-DSC. The characterization of those photolytic and thermolytic products of bridged alkylcobaloximes shows that the carbon-center radical which is produced from the Co–C bond cleavage may

link to the equatorial ligand and be retained in the proximity of Co^{II} -complex.

Experimental section

Caution: The perchlorates are potentially explosive. Only a small amount of material should be prepared at any one time and it should be handled with care. All manipulations for treating were performed in the dark to avoid Co–C bond cleavage. All chemicals used were of analytical reagent grade unless stated otherwise. Aqua-(3-bromopropyl)cobaloxime **1** was prepared by reductive alkylation as described in the literature.²⁷

Complex **2** (Fig. 1) was prepared by heating aqua(3-bromopropyl)cobaloxime (complex **1**) at 80 °C in water through an intra-molecular nucleophilic substitution reaction.

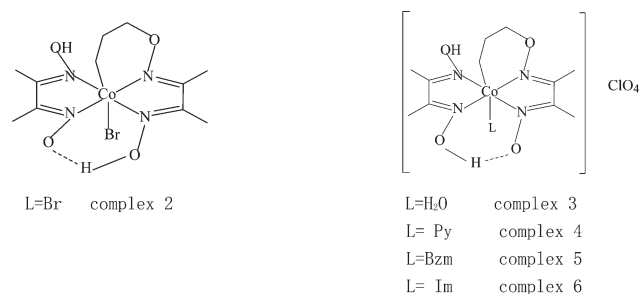


Fig. 1 Schematic representation of the intramolecular bridged alkyl cobaloxime complexes.

For complexes **3–6** (Fig. 1), the axial ligand Br of complex **2** was removed by adding AgNO_3 first. Then new L ligand (L = H_2O for **3**, L = Py for **4**, L = Bzm for **5**, L = Im for **6**) coordinated with $\text{Co}(\text{III})$ and gave a cation which combined with the ClO_4 anion produced the relevant complexes.²⁶

Photolysis

All samples for photolysis were prepared in aqueous solutions at 25 °C under anaerobic conditions and red light. The solution of concentration about 10^{-3} M was loaded into a quartz cuvette (1 cm path length) and degassed for 30 min by vigorous bubbling of nitrogen gas through it. Lastly the cuvette for the anaerobic sample was sealed with a Teflon cap under positive nitrogen pressure, and exposed to five 8 W white light lamps, which were placed cylindrically at a distance of 20 cm.

The absorbance changes of the UV-Vis spectra during photolysis were recorded by UV/3100.

Table 1 The assignment for peaks of complex **2**

Mass charge ratio (<i>m/z</i>)	Relative abundance	Assigned species
289.2	65	[M ₁₂ - Br] ⁺
329.8	39	[M ₁₀ - Br] ⁺
367.9	100	[M ₉ - Br + 2H ₂ O] ⁺
399.7	56	[M ₉ - Br + 2H ₂ O + CH ₃ OH] ⁺
619.0	43	[(M ₁₀ - Br) + (M ₁₁ - Br)] ⁺
650.8	64	[(M ₁₀ - Br) + (M ₁₁ - Br) + CH ₃ OH] ⁺

The photolytic kinetic measurements were performed under pseudo-first-order conditions and the reactions followed at least 3 half-lives. The observed rate constants were calculated by linear least-squares regression using the formula:

$$\ln \frac{A_0 - A_\infty}{A_t - A_\infty} = kt.$$

The ESI-MS measurements of photolysis products of all the complexes were carried out on a LCQ-Finnigan at room temperature. The mobile phase is methanol/water (1:1). Photolytic samples for the ¹H-NMR analysis were prepared in anaerobic D₂O solution and the conditions are similar to those for other photolysis measurements. After a certain time, the photolytic reaction mixture was oxidized by bubbling through O₂ and ¹H-NMR spectra were determined by using the 500-MHz Bruker spectrometer with DSS as internal reference.

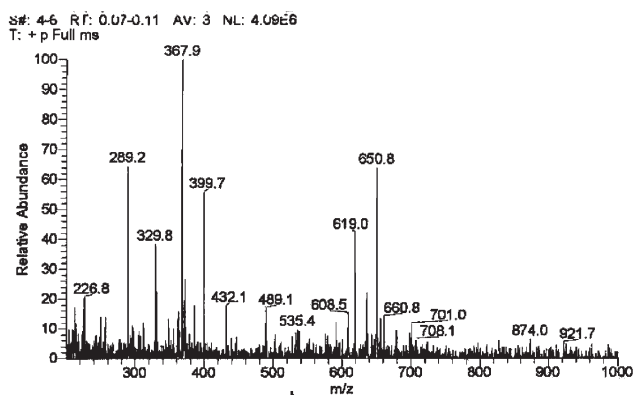
Thermal analysis

The TG and DSC curves of complex **2** were recorded on LabsysTMTG-DSC16 thermal analyzer at a heating rate of 10 °C min⁻¹ in a flowing nitrogen atmosphere from 25 to 500 °C. Al₂O₃ was used as the reference material.

Results and discussion

Photolysis of the bridged complexes

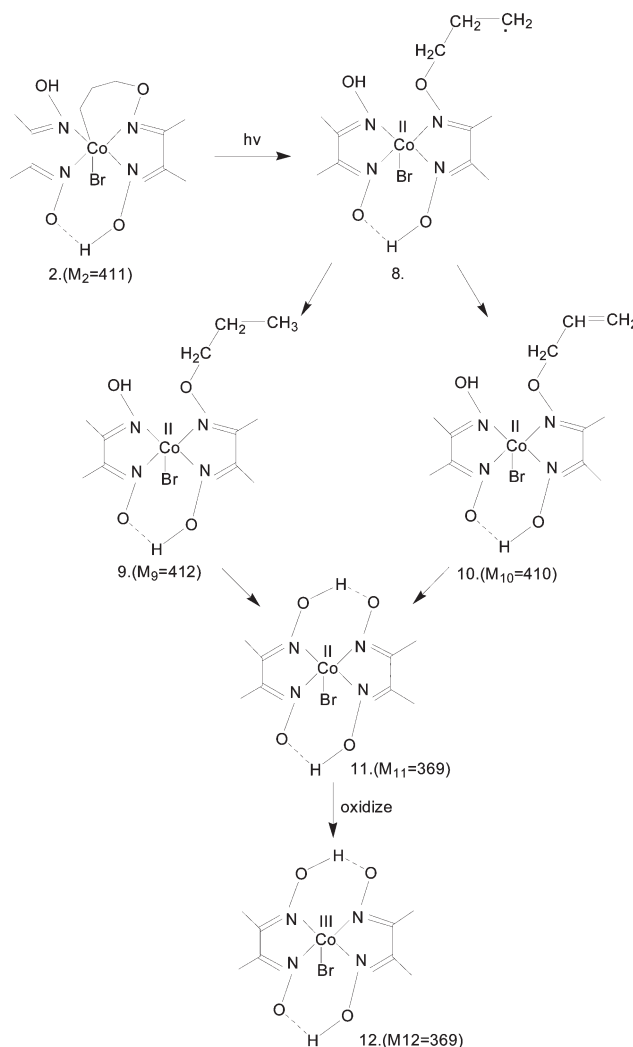
1. ESI-MS investigation of the photolytic solution. The photolytic solution of complex **2** was examined by ESI-MS. There are six intense peaks in its spectrum after 5 h of photolysis (Fig. 2) and their assignments were summarized in Table 1. The most intense signal at *m/z* 367.9 can be assigned to the [M₉ - Br + 2H₂O]⁺, *i.e.* adduct of two waters and the de-bromine Co(II)oxime derivative (species **9**), which has a propyl side-chain connected to oxime-oxygen in an equatorial plane. The peak at *m/z* 329.8 corresponds to [M₁₀ - Br]⁺, *i.e.* a de-bromine Co(II)oxime derivative (species **10**), which has an allyl side-chain connected with oxime-oxygen in an equatorial plane, and the peak at *m/z* 289.2 may be assigned to de-bromine bis(dimethylglyoximate)cobalt(III) [M₁₂ - Br]⁺. The peaks at *m/z* 399.7, 619.0, and 650.8 were assigned to adducts of two or more species respectively (see Table 1).

**Fig. 2** ESI-MS spectrum for photolytic products of complex **2**.**Table 2** The assignment for peaks of complex **4**

Mass charge ratio (<i>m/z</i>)	Relative abundance	Assigned species
289.2	100	[M ₁₅ - Py] ⁺
367.9	74	[M ₁₃ - Py + 2H ₂ O] ⁺ or [M ₁₅] ⁺
399.7	42	[M ₁₃ - Py + 2H ₂ O + CH ₃ OH] ⁺ or [M ₁₅ + CH ₃ OH] ⁺

In summing, all peaks detected are de-bromine or solvent adding species, which were formed under the ESI experimental conditions.

According to the experimental results, the products are a mixture of various cobalt species and the photolytic mechanism for complex **2** in Scheme 1 has been postulated. First, after Co-C bond homolysis of complex **2** a carbon-centered radical, which linked to the N-O bond of the equatorial ligand by a -(CH₂)₃ bridge, was formed. This original organic radical then undergoes abstraction or captures an H²⁸ atom to form two intermediate products **9** and **10**, *i.e.* propyl-Co(II)oxime and allyl-Co(II)oxime derivative, respectively. Next, the C-O bond of two intermediate products was cleaved to give product **11**. Last, Co(II) of product **11** was oxidized to form Co(III) species **12**.

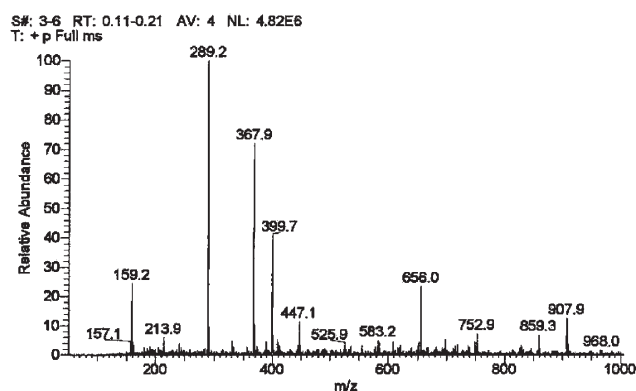
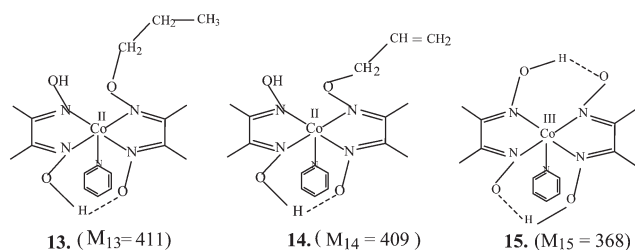
**Scheme 1** The proposed photolytic mechanism for complex **2**.

ESI-MS spectrum of photolytic solution of complex **4** is shown as Fig. 3. It can be seen that (Figs. 2 and 3) all have the peaks at *m/z* 367.9 and 289.2, but there is no peak at *m/z* 329.8 in the photolytic product of complex **4**. We have assigned the peak at *m/z* 367.9 to the adduct of species **9** (de-bromine propyl-Co(II)oxime species) and 2H₂O in the photolytic

Table 3 The assignment for peaks in complex 5

Mass charge ratio (<i>m/z</i>)	Relative abundance	Assigned species
289.1	78	[M ₁₆ – Bzm] ⁺
406.9	100	[M ₁₆] ⁺
438.6	50	[M ₁₆ + CH ₃ OH] ⁺
524.9	100	[M ₁₆ + Bzm] ⁺

product of complex 2, but now we cannot assign this peak clearly, because both species [M₁₅]⁺ and [M₁₃ – Py + 2H₂O]⁺ have the same mass-to-charge ratio. According to the previous study of the photolytic product of alkylcobaloximes,¹¹ it was found that the carbon-centred radical formed after homolysis of the Co–C bond may change to the alkene derivative and alkane derivative at the same time. For the allyl-Co(II)oxime derivative, *i.e.* peak at *m/z* 330.0 ([M₁₄ – Py]⁺) was not observed, we tended to assign the peak at *m/z* 367.9 to [M₁₅]⁺. Considering the axial Py ligand is easy to lose in the process of ESI-MS,²⁶ we could not dismiss that the peak at *m/z* 367.9 corresponds to [M₁₃ – Py + 2H₂O]⁺. All peak assignments were listed in Table 2 and the photolytic mechanism of complex 4 is considered to be the same as complex 2.

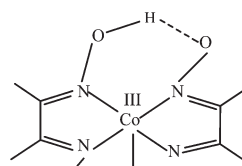
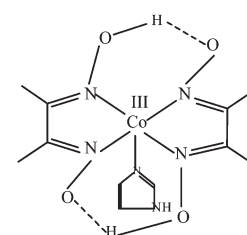
**Fig. 3** ESI-MS spectrum for photolytic products of complex 4.

The ESI-MS spectrum of photolytic solutions of complexes 5 and 6 are shown in Fig. 4, and the peak assignments are listed in Tables 3 and 4. In the photolytic products of these two complexes, neither of the allyl-Co(II)oxime and propyl-Co(II)oxime intermediate products could be found. Only the

Table 4 The assignment for peaks in complex 6

Mass charge ratio (<i>m/z</i>)	Relative abundance	Assigned species
289.2	21	[M ₁₇ – Im] ⁺
425.1	100	[M ₁₇ + Im] ⁺

species involving M₁₆ or M₁₇ were observed. It may be due to the more electronic donating ability of the axial L ligand and lower stability of the C–O bond. Therefore, the intermediate products could not be identified in the photolytic products of their two complexes.

**16.** (M₁₆ = 407)**17.** (M₁₇ = 357)

The photolysis products of complex 3 are different from the other complexes and we cannot explain them clearly now.

2. ¹H-NMR characterization of photolytic solution 2. In order to verify the results described above, photolysis of our bridged complex in D₂O was monitored by ¹H-NMR. As an example, before photolysis the original spectrum of complex 2 showed four single peaks for oxime-methyl at 2.25–2.57 ppm. The methylene protons located on a six membered ring between the Co(III) and oxime-O atom appear at 4.75 and 3.92 for H(9); 2.59 and 1.91 for H(11); 1.66 and 0.52 for H(10) respectively.²⁶ It indicates that the non-equivalence both for the four CH₃ at oximes and two protons of each methylene on six membered rings. After 5 h photolysis of the sample in D₂O, it was oxidized, and new signals appeared on the ¹H-NMR spectrum except for the old peaks of complex 2. The complexity of the spectrum shows that the photolytic products are a mixture of Co(III) species. We suggest that those new peaks at lower field (5–6 ppm) and higher field (1–2 ppm) could be assigned to the signals of allyloxyl (CH₂=CH–, –CH₂–O–) in complex 10' and propoxyl (–CH₂–O–, –CH₂–, CH₃–) of complex 9', which are both the oxidized Co(III) products, respectively. Based on the integration and comparison, the new multiple-peaks at about 2.1 ppm could be assigned to the CH₃– of oxime planes of species 9' and 10'. The single peak around 2.3 ppm is to assigned to oxime CH₃– of species 12. With prolonged photolysis, the signals of complex 2 decreased and signals of complex 10' and 12 increased. Therefore, the results of the ¹H-NMR study for photolysis of complex 2 can provide more evidence for the photolytic mechanism postulated by the ESI-MS.

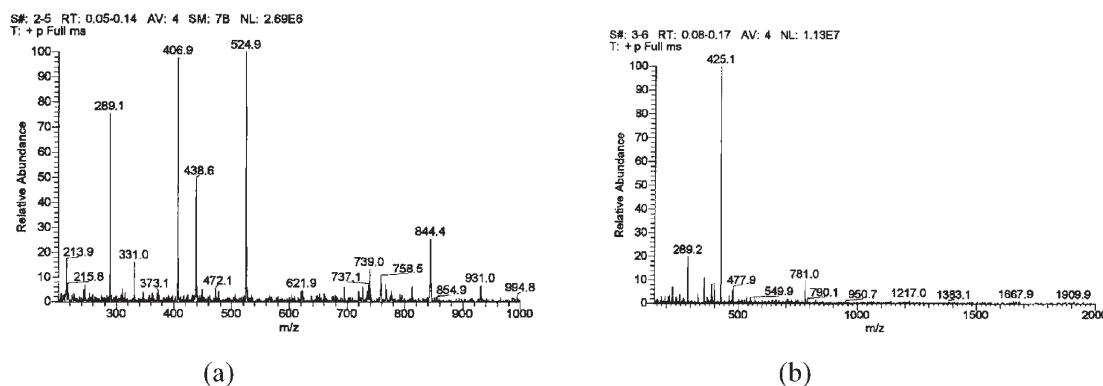
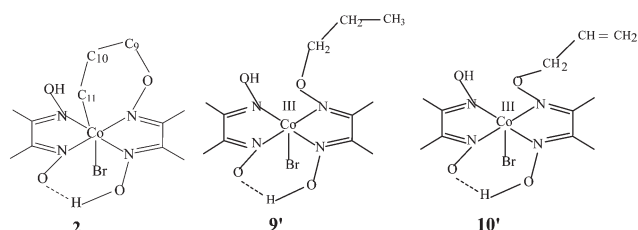
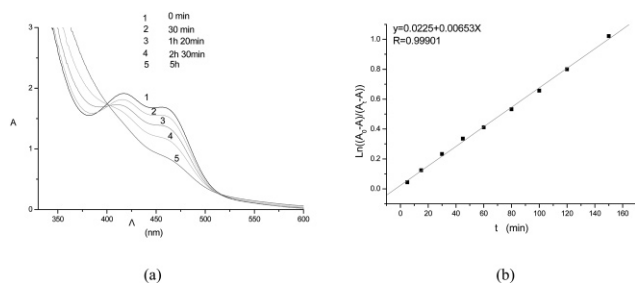
**Fig. 4** ESI-MS spectrum of photolytic products of complex 5 (a) and 6 (b).

Table 5 The observed photolytic rate constants for complexes 1–6

	1	2	3	4	5	6
Observed rate constant/min ⁻¹	7.56×10^{-2}	6.53×10^{-3}	1.99×10^{-2}	1.79×10^{-2}	1.21×10^{-2}	6.83×10^{-3}
$T_{1/2}$ /min	9.17	106	34.8	38.7	57.3	101



2. Kinetic studies. The absorbance change of UV-Vis in photolysis and the plot of the observed rate constant for complex **2** are shown in Fig. 5. It was seen that absorbances at 419.0 nm and 452.8 nm gradually decrease and the decomposition process of the Co–C bond obeys a pseudo-first-order rate law.

**Fig. 5** UV-Vis change (a) and the observed rate constant (b) for complex **2**.

Through UV-Vis study, we determined the observed rate constants in photolysis of all intramolecular bridged alkyl cobaloximes (complexes **2–6**) and their precursor aqua-(3-bromopropyl)cobaloxime (complex **1**). Data are shown in Table 5:

It is observed that:

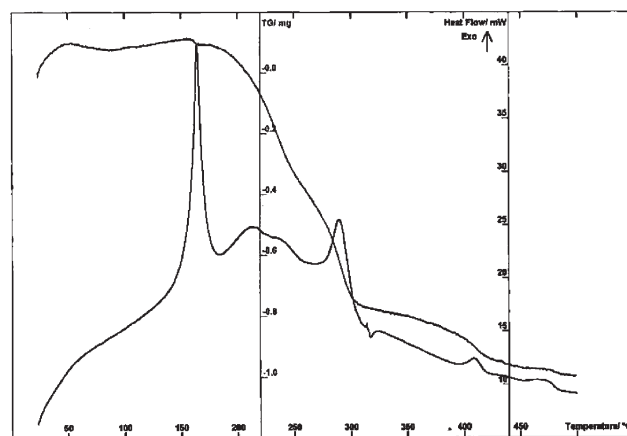
(a). The observed rate constants of the bridged alkylcobaloximes are smaller than that of aqua-(3-bromo-propyl)-cobaloximes. Probably the carbon-center radical produced by the Co–C bond cleavage in photolysis was linked to the equatorial ligand and retained in the proximity of Co^{II}-complex for intramolecular bridged alkyl cobaloxime complexes. Thus the recombination reaction between Co^{II}-complex and carbon-center radical is easier to proceed as compared to the non-bridged complexes.^{5,15–18}

(b). In our bridged alkylcobaloximes, the observed photolytic rate constants increase with decreasing pK_a values of the L ligands, i.e. $K_{obs,Py}(pK_a = 5.25) > K_{obs,Bzm}(pK_a = 5.53) > K_{obs,Im}(pK_a = 6.95)$, when the bases have the same coordinate atom (N). A reasonable explanation for this trend is that the more basic ligands are expected to stabilize the parent cobalt(III)-alkyl relative to the cobalt(II) dissociation product and hence to increase the bond dissociation energy.²⁹

TG and DSC analysis

TG and DSC scans for complex **2** are displayed in Fig. 6. There is almost no weight change in the TG scan from 50–150 °C, except the slight weight increasing before 50 °C. While in the temperature range of 150–500 °C the complex has a continuous weight-loss (26.93%). This process corresponds to a loss in an axial Br ligand and a part of methylene in the bridge (for loss one Br and C₃H₆; calc. 29.65%). It is also noted that all the corresponding peaks of DSC are exothermic. Comparing to studies of other alkylcobaloximes³⁰ the thermal decomposition

property of complex **2** has a different character. There is a strong exothermic peak in the DSC scan at 150 °C but there is almost no corresponding weight-loss in TG. This not significant weight-loss (only 0.417%) is probably due to the fact that one H atom was lost from the carbon-center radical to form a C=C species after Co–C bond cleavage, and the allyl is still linked to the equatorial ligand. In addition, the value change in the DSC scan (136.88 kJ mol⁻¹, exothermic) is very close to that previously determined for the Co–C bond dissociation energy in the literature.³¹

**Fig. 6** TG and DSC curves for complex **2**.

As there are perchlorates in complexes **3–6**, TG-DSC experiments cannot be performed.

Conclusion

In this work, the interesting photolytic and thermal properties of a new series of intramolecular bridged alkyl cobaloximes complexes have been investigated. The results are summarized as follows.

(a). The observed rate constants of the bridged alkylcobaloximes are smaller than that of aqua-(3-bromo-propyl)cobaloximes, and the observed rate constants in photolysis increase with decreasing axial L ligand's pK_a .

(b). The characterization of the photolytic products of bridged alkylcobaloximes suggest that the carbon-center radical, which is produced from Co–C bond cleavage, may be linked to the equatorial ligand and retained in the proximity of the Co^{II}-complex. TG-DSC analysis also provides such information. Therefore, this kind of organocobalt complex may mimic the Co–C bond property at holo-enzyme and become a type of novel coenzyme B₁₂ model.

Acknowledgements

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