Spin trapping EPR investigation of the photolysis of aqua(alkyl)-cobaloximes: 1,2-rearrangement reactions of photo-induced primary radicals and β-cyclodextrin's stabilizing effects†

Xinyi Song, Ying Chen and Huilan Chen*

Department of Chemistry and State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, P. R. China

Received (in Montpellier, France) 11th December 2000, Accepted 11th April 2001
First published as an Advance Article on the web 14th June 2001

The radicals formed from photolysis of aqua(alkyl)cobaloximes (R = *sec*-C_4H_9, *n*-C_4H_9, *i*-C_4H_9, *c*-C_5H_9 or *c*-C_6H_{11}) in the absence and presence of β-cyclodextrin at room temperature have been characterized by the EPR spin trapping technique using 2-methyl-2-nitrosopropane. It has been found that only the primary alkyl radicals produced by Co–C bond cleavage of the cobaloximes during photolysis undergo 1,2-rearrangement reactions. The spin adducts formed can be included in the cavity of β-cyclodextrin, which plays an important role in stabilizing the primary alkyl radicals.

Introduction

Alkylcobaloxime, which is an organometallic complex containing a σ-type Co–C bond, has been investigated extensively as an important model for coenzyme B_{12} (5′-deoxyadenosylcobalamin).[1] It is generally accepted that homolysis of the Co–C bond in coenzyme B_{12} induced by enzyme protein to produce a 5′-deoxyadenosyl radical is the key step in the B_{12}-dependent enzymatic reactions.[2] In these reactions the substrate undergoes 1,2-interchange of a hydrogen atom and a substituent on the adjacent carbon atom. Many investigations on the photolysis of coenzyme B_{12} and its model compounds have been undertaken since they might simulate the behavior of either the 5′-deoxyadenosyl radical released in the enzymatic reactions or the radical intermediates formed between substrate and product.[3] During the last few decades a radical mechanism *via* a three-membered cyclic transition state had been proposed for these rearrangement reactions.[4a,b] Recently other mechanisms such as ionic reaction have also been suggested.[4c,d] However, further investigations are needed to clarify the mechanism.

The EPR spin trapping technique is a powerful method of detecting the presence of short-lived radicals.[5] Some ordinary spin traps, such as *N*-*tert*-butyl-α-phenylnitrone (*N*-*tert*-butyl benzylidene *N*-oxide) (PBN) or 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO), can not directly provide structure information on the trapped radicals because the latter are not connected to the ^{14}N atoms of the trapping agents. On the other hand 2-methyl-2-nitrosopropane (MNP) traps the radical R$^\bullet$ forming a direct linking adduct RN(O$^\bullet$)-*t*-C_4H_9 between the radical and the ^{14}N atom, and gives further hyperfine splitting of the magnetic nuclei around the ^{14}N.

Nonetheless, MNP has its own disadvantages: poor solubility in water, and the majority of it exists in the inactive dimeric state. We had found that the above deficiency could be ameliorated by adding β-cyclodextrin (β-CD) because β-CD catalyzes decomposition of the dimeric state of MNP into the monomer effectively and enhances its solubility.[6] It is also well known that β-CD can include a variety of organic molecules and inorganic ions into its cavity.[7] There are also various reports on the inclusion complexes of β-CD with neutral or charged radicals such as nitroxide radicals,[8] methyl viologen radical cation and dicyanobenzene radical anion.[9,10] Previously, by using MNP as a trap we have studied the photolysis of some organocobalt complexes with simple alkyl ligands and characterized the released radicals.[11] No 1,2-rearrangements of alkyl radicals were found in these photolytic reactions except for few cases in our recent works in the absence of β-CD.[11d] However, further investigations are needed on the influence of β-CD and the 1,2-rearrangements of the photo-induced alkyl radicals arising from Co–C bond cleavage of different kinds of organocobalt model compounds.

In this paper by using MNP as spin trap we have studied the photolysis of different kinds of aqua(alkyl)cobaloxime aqueous solutions [CoR(DH)$_2$(H$_2$O), R = *sec*-C_4H_9, *n*-C_4H_9, *i*-C_4H_9, *c*-C_5H_9 or *c*-C_6H_{11}, DH = dimethylglyoximate] at room temperature in the absence and presence of β-CD. We found 1,2-rearrangement reactions for the primary alkyl radicals produced by Co–C bond cleavage of these complexes and that β-CD could stabilize them to a certain extent.

Experimental

MNP was prepared according to the method suggested by Stowell.[12] β-CD was supplied by Nanjing Food Ferment Institute, recrystallized twice from distilled water and dried *in vacuo* at 80 °C. CoR(DH)$_2$(H$_2$O) (R = *sec*-C_4H_9, *n*-C_4H_9, *i*-C_4H_9, *c*-C_5H_9 or *c*-C_6H_{11}) were synthesized according to the literature.[13] The purity was ascertained by ^{1}H NMR and elemental analysis.

EPR measurements were carried out on a JEOL-FE1XG spectrometer at room temperature with 100 kHz field modulation, 0.5 G modulation width, 5 mW microwave power, 9.45

---

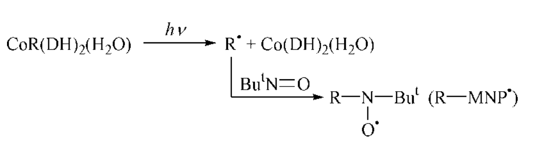
† Electronic supplementary information (ESI) available: experimental and simulated EPR spectra obtained upon photolysis of aqua(alkyl)cobaloximes. See http://www.rsc.org/suppdata/nj/b0/b009972o/

DOI: 10.1039/b009972o

GHz microwave frequency and 0.1 s response time. Irradiation was performed in the cavity of the EPR spectrometer using a BM-501S high-pressure mercury lamp with a wavelength in the ultra-violet range. Samples were prepared under dim red lights and injected into a flat quartz sample tube (0.5 × 4.2 × 43.5 mm). The aqueous solution in the absence of β-CD contained 2×10^{-2} mol dm^{-3} $CoR(DH)_2(H_2O)$ and 6×10^{-2} mol dm^{-3} MNP aqueous solution, the latter being prepared by adding 25 mg MNP to 5 cm^3 redistilled water with continuous stirring for 4 h at 45 °C under nitrogen. The sample in the presence of β-CD contained 1×10^{-2} mol dm^{-3} $CoR(DH)_2(H_2O)$, 2×10^{-2} mol dm^{-3} MNP and 2×10^{-2} mol dm^{-3} β-CD aqueous solution. EPR simulation was performed using the Bruker WINEPR program.

Results and discussion

According to previous reports, short-lived alkyl radicals can arise during photolysis of aqua(alkyl)cobaloximes.[13] They can undergo further reactions such as dimerization, disproportionation or recombination with the photo-induced cobalt(II) ions, *etc.*[3c,d,14] In the presence of MNP, the stable spin adducts R–MNP are formed [eqn. (1)].[15]



$$CoR(DH)_2(H_2O) \xrightarrow{h\nu} R^{\bullet} + Co(DH)_2(H_2O) \qquad \xrightarrow{Bu^tN=O} R\text{–}\underset{\displaystyle O^{\bullet}}{\underset{|}{N}}\text{–}Bu^t \ (R\text{–}MNP^{\bullet}) \qquad (1)$$

In this work we have studied the photolysis of three butyl and two cycloalkyl cobaloximes through EPR spin trapping using MNP as trap in the absence and presence of β-CD.

Photolysis of $Co(sec\text{-}C_4H_9)(DH)_2(H_2O)$

The EPR spectrum obtained by photolysis of $Co(sec\text{-}C_4H_9)(DH)_2(H_2O)$ in the presence of MNP is shown in Fig. 1 which contains two sets of signals. One set is considered to arise from the spin adduct between $sec\text{-}C_4H_9^{\bullet}$ and MNP. It contains three peaks with equal intensity ($a_N = 1.68$ mT) and is split further into double peaks ($a_H = 0.18$ mT), attributed to one H_β on the C_α atom adjacent to the ^{14}N nucleus. Usually the values of a_H for spin adducts of secondary alkyl radicals with MNP are 0.1–0.2 mT and for primary radical adducts with MNP the values are 1.0–1.1 mT, changing a little in some common solvents.[6,11a,16] So the structure of alkyl spin adducts can be determined not only from the number of EPR peaks, but also from their values of a_H. This confirms further our assignments of the above $sec\text{-}C_4H_9$–MNP and other adducts whose hyperfine splitting constants are listed in Table 1.

In the presence of β-CD the photolysis EPR spectrum of $Co(sec\text{-}C_4H_9)(DH)_2(H_2O)$ using MNP as trap (see ESI) is similar to the spectrum in Fig. 1, whilst a_N (1.62 mT) is smaller than that for free alkylcobaloxime (1.68 mT). From previous investigations of spin trapping EPR using aminoxyl radicals as scavengers it has been found that EPR parameters are sensitive to the environment and the values of a_N could reflect the polarity around the aminoxyl group, *i.e.* the more polar the media the larger the value of a_N.[8] Comparing the a_N values of $sec\text{-}C_4H_9$–MNP, in the presence of β-CD the spin adduct could be in a less polar environment than in pure water. Apparently, it is included into the hydrophobic cavity of β-CD according to our previous investigations and others.[6,8] Meanwhile, the three doublet signals lose their symmetry with a marked broadening of the highest field peak ($m_I = -1$). Such a line broadening is attributed to slow rotation of the guest in the β-CD cavity. This provides further evidence for the formation of an inclusion complex between β-CD and R-MNP.[8,17]

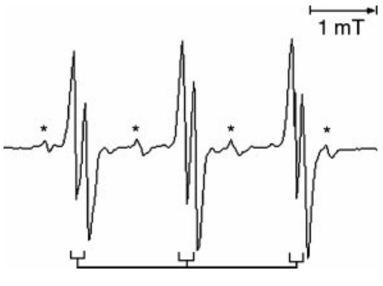


Fig. 1 The EPR spectrum upon photolysis of $Co(sec\text{-}Bu)(DH)_2$ $H_2O)$ and MNP in water.

Table 1 The EPR parameters for free and included radical adducts detected in aqueous media at room temperature

Radical		g^a	$a_N{}^b$/mT	a_H or $a_D{}^b$/mT
$sec\text{-}C_4H_9$–	Free	2.0056	1.68	0.18
MNP	β-CD	2.0057	1.62	0.18
$n\text{-}C_4H_9$–	Free	—	—	—
MNP	β-CD	2.0058	1.64	1.00
$i\text{-}C_4H_9$–	Free	2.0057	1.68	1.13
MNP	β-CD	2.0058	1.62	1.01
$c\text{-}C_5H_9$–	Free	—^{c}	1.69	—^{c}
MNP	β-CD	—^{c}	1.62	—^{c}
$c\text{-}C_6H_{11}$–	Free	—^{c}	1.67	—^{c}
MNP	β-CD	—^{c}	1.60	—^{c}
H–MNP	Free	2.0058	1.44	1.40
	β-CD	2.0059	1.40	1.29
D–MNP	Free	2.0058	1.44	0.22
(in D_2O)	β-CD	2.0059	1.40	0.20

^{a} Error is ±0.0001. ^{b} Error is ±0.01 mT. ^{c} Not resolved.

Another set of signals in Fig. 1 and the features marked * will be discussed later.

Photolysis of $Co(n\text{-}C_4H_9)(DH)_2(H_2O)$

The photolysis EPR spectrum of $Co(n\text{-}C_4H_9)(DH)_2(H_2O)$ with MNP is shown in Fig. 2(a). We did not observe the expected signals of $n\text{-}C_4H_9$–MNP, which should be a set of three peaks with equal intensity and split further into triplets with intensity 1 : 2 : 1, but a set similar to that of $sec\text{-}C_4H_9$–MNP both in peak shape and in g value. An identical spectrum was obtained when solutions of $Co(n\text{-}C_4H_9)(DH)_2(H_2O)$ and $Co(sec\text{-}C_4H_9)(DH)_2(H_2O)$ were blended and photolyzed

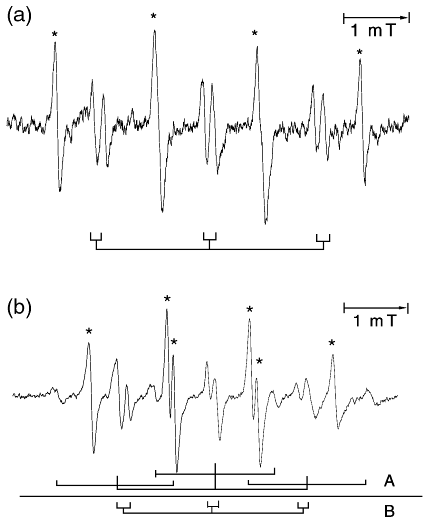


Fig. 2 The EPR spectra for photolysis of $Co(n\text{-}Bu)(DH)_2(H_2O)$ and MNP in water (a) and in the presence of β-CD in water (b).

together (see ESI). This suggests the trapped radical in Fig. 2(a) could be *sec*-$C_4H_9^{\cdot}$ which comes from a 1,2-hydrogen shift from the precursor *n*-$C_4H_9^{\cdot}$ radical generated *via* photolysis of Co(*n*-C_4H_9)$(DH)_2(H_2O)$ (Scheme 1).

To our knowledge the stability of alkyl radicals is primary < secondary < tertiary. So the photo-induced *n*-$C_4H_9^{\cdot}$ could be very active and part might transform into *sec*-$C_4H_9^{\cdot}$ before being captured. Although in pure organic systems the rate of 1,2-rearrangement is so small that the rearrangement products can not be detected,[18] in many cases these rearrangements for coenzyme B_{12} model compounds during photolysis did occur in the presence of cobalt(II) species.[19] Our results provide another example of alkyl rearrangement reactions in organocobalt complexes.

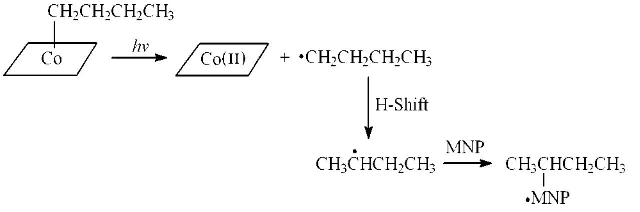
The smaller signal intensity of *sec*-C_4H_9–MNP in Fig. 2(a) might be attributed to instability of the produced *n*-$C_4H_9^{\cdot}$ most of which would have been quenched before the rearrangement reaction had occurred as we mentioned above.

However, in the presence of β-CD the photolysis EPR spectrum of Co(*n*-C_4H_9)$(DH)_2(H_2O)$ with MNP [see Fig. 2(b)] gives two sets of signals. One contains three 1 : 2 : 1 split peaks (A) with a_N of 1.64 mT which could be the expected signal for *n*-C_4H_9–MNP, which is included by β-CD. The other set of three doublets with smaller intensity (B) could be derived from the rearrangement reaction, which is also included. Obviously, β-CD has a function of stabilizing primary radicals such as *n*-$C_4H_9^{\cdot}$ and its spin adduct can be detected during photolysis.

Photolysis of Co(*i*-C_4H_9)$(DH)_2(H_2O)$

The photolysis EPR spectrum of Co(*i*-C_4H_9)$(DH)_2(H_2O)$ with MNP is shown in Fig. 3(a). As expected there are of 3 × 3 peaks (A) but their intensity deviates from 1 : 2 : 1. The reason may be that the produced *i*-$C_4H_9^{\cdot}$ is also a primary radical and it might partially undergo 1,2-rearrangement reactions (Scheme 2). On one hand, a 1,2-methyl shift generates a rearrangement product *sec*-$C_4H_9^{\cdot}$. Its adduct (B) partially overlaps the *i*-C_4H_9–MNP signals. On the other hand, a 1,2-hydrogen shift gives *t*-$C_4H_9^{\cdot}$ which can be produced more easily than *sec*-$C_4H_9^{\cdot}$. The former combines with MNP to form *t*-C_4H_9–MNP, *i.e.* di-*tert*-butylaminoxyl (DTBA). However, its three single peaks (C) might be overlapped by the three strong central signals of *i*-C_4H_9–MNP if it exists. From computer simulation [see Fig. 3(b)] we got a similar spectrum only when the above presumption was applied. Therefore, using MNP as trap we could detect *i*-$C_4H_9^{\cdot}$ and its 1,2-rearrangement products during photolysis of its cobaloxime precursor.

In the presence of β-CD the photolysis EPR spectrum of Co(*i*-C_4H_9)$(DH)_2(H_2O)$ with MNP shows three sets of signals [Fig. 3(c)]. One set of three triplets is derived from the inclusion complex of *i*-C_4H_9–MNP and β-CD (a_N = 1.62 mT). Another set having three single peaks marked ○ with a_N of 1.67 mT comes from DTBA/β-CD.[11] It is apparent that the 1,2-hydrogen shift of *i*-$C_4H_9^{\cdot}$ could occur readily to form the fairly stable radical *t*-$C_4H_9^{\cdot}$, so we did not find the methyl-shift peaks which should be similar to that of *sec*-$C_4H_9^{\cdot}$. We obtained a similar spectrum to the experimental one by computer simulation (see ESI) using the EPR parameters of only these two species and H–MNP/β-CD (see below). It indicates that probably in the presence of β-CD the 1,2-methyl shift reaction was hindered to a certain extent, *i.e.* β-CD can stabilize the produced *i*-$C_4H_9^{\cdot}$ by skeletal rearrangement.



Scheme 1 H-atom rearrangement.

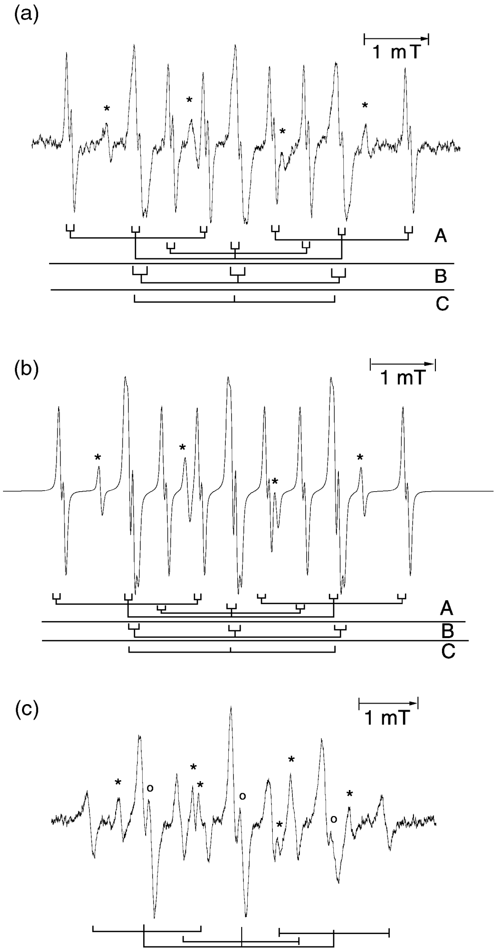
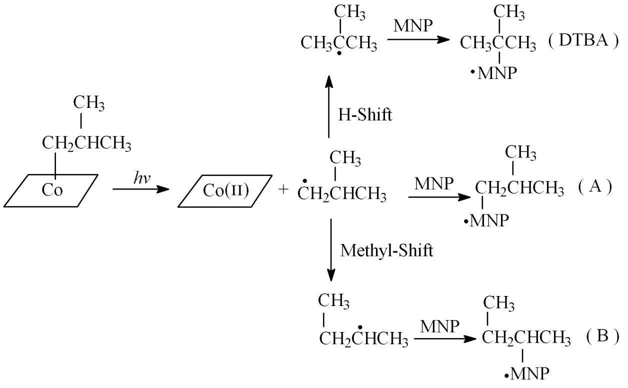


Fig. 3 The EPR spectrum upon photolysis of Co(*i*-Bu)$(DH)_2(H_2O)$ and MNP in water: (a) experimental, (b) simulated and (c) in the presence of β-CD. Upon simulation the signals of *i*-Bu–MNP, *sec*-Bu–MNP, *t*-Bu–MNP and H–MNP merged.

The third set marked * in Fig. 3(c) and in all above spectra with triple 1 : 1 peaks is assigned to H–MNP (a_N = 1.44, a_H = 1.40 mT) or its inclusion complex with β-CD (a_N = 1.40, a_H = 1.29 mT) which are confirmed by comparison with EPR data from the literature (a_N = 1.445 and a_H = 1.40 mT in aqueous solution).[20] Owing to their instability, they disappear using continuous illumination or shutdown of the lamp. It is interesting to get 3 × 3 peaks with equal intensity for D–MNP when the experiment was performed in D_2O (see ESI). According to a previous report the trapped radical $H^{\cdot}$ is from the equatorial ligands of cobaloxime.[21] So our experiments



Scheme 2 H-atom and methyl rearrangements.

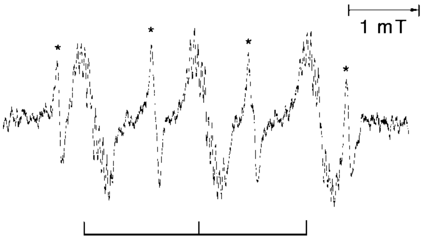


Fig. 4 The EPR spectrum upon photolysis of Co(c-C_5H_9)-$(DH)_2(H_2O)$ and MNP in water.

indicate that the H˙/D˙ may come from the hydrogen/deuterium of the equatorial oxime which can rapidly exchange protons with the solvent.

Photolysis of Co(c-C_5H_9)$(DH)_2(H_2O)$

The photolysis EPR spectrum of Co(c-C_5H_9)$(DH)_2(H_2O)$ with MNP is shown in Fig. 4. Though c-$C_5H_9^{\cdot}$ is a secondary radical, it did not give the typical EPR signals with 1 : 1 splitting but multiple overlapping ones similar to those of the spin adduct from succinimidyl and MNP.[5] The multiple splitting is attributed to the interplay from H atoms in the cycloalkyl skeleton.[5,22] Deuterium-labeling experiments are needed to resolve the overlapping spectra. In the presence of β-CD the spectrum (see ESI) showed poorer resolution and was different from Fig. 4. The broadening of the highest field peak and smaller value of a_N could verify the inclusion of the spin adduct.

The photolysis EPR spectra of Co(c-C_6H_{11})$(DH)_2(H_2O)$ with MNP in the absence and presence of β-CD are similar to those above (see ESI). The signals of H–MNP and H–MNP/β-CD are also found in these spectra.

The characters of the two cycloalkyl radical adducts are quite different from acyclic ones and no signals of rearrangement products were detected for these cycloalkyl precursors.

Conclusion

A photolysis spin trapping EPR investigation of aqua(alkyl)cobaloximes (R = i-C_4H_9, sec-C_4H_9, n-C_4H_9, c-C_5H_9 or c-C_6H_{11}) in the absence and presence of β-CD using MNP as radical trap has been performed. Our results indicate that only the 1,2-rearrangement adducts for *primary* alkyl radicals could be detected as n-$C_4H_9^{\cdot}$ undergoes a 1,2-hydrogen shift solely while i-$C_4H_9^{\cdot}$ exhibits both 1,2-hydrogen and 1,2-methyl shifts. We have not detected such products in the secondary acyclic or cyclic alkyl precursors. In the presence of β-CD the radicals can be included into the β-CD cavity and the above 1,2-shift reactions are hindered to a certain extent. To our knowledge, there are few reports on radical rearrangements on homolysis of the Co–C bonds of alkylcobalt complexes studied by the EPR spin trapping technique. So our method, especially using MNP as spin trap, may offer some convenience in this field. Further studies are in progress.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (no. 29823001 and 20071017) and the Research Fund for the Doctoral Program of Higher Education (no. 2000028401).

References

1 N. Bresciani-Pahor, M. Forcolin, L. G. Marzilli, L. Randaccio, M. F. Summers and P. J. Toscano, *Coord. Chem. Rev.*, 1985, **63**, 1; L. Randaccio, N. Brescini Pahor, E. Zangrando and L. G. Marzilli, *Chem. Soc. Rev.*, 1989, **18**, 225.

2 J. Halpern, *Science*, 1985, **227**, 869 and refs. therein; J. M. Pratt, *Chem. Soc. Rev.*, 1985, **14**, 161.

3 (*a*) J. M. Pratt, *Inorganic Chemistry of Vitamin B_{12}*, Academic press, New York, 1976; (*b*) J. F. Endicott and T. L. Netzel, *J. Am. Chem. Soc.*, 1979, **101**, 4000; (*c*) E. Chen and M. R. Chance, *J. Biol. Chem.*, 1990, **265**, 12987; (*d*) E. Chen and M. R. Chance, *Biochemistry*, 1993, **32**, 1480 and refs. therein; (*e*) *Vitamin B_{12} and B_{12}-Proteins*, ed. B. Krautler, D. Arigoni and B. T. Golding, Wiley-VCH, Weinheim, 1998; (*f*) *Chemistry and Biochemistry of B_{12}*, ed. R. Banerjee, Wiley, New York, 1999.

4 (*a*) M. A. McKervey, J. J. Rooney and N. G. Samman, *J. Catal.*, 1973, **30**, 330; (*b*) L. Salem, O. Eisenstein, N. T. Anh, H. B. Burgi, A. Devaquet, G. Segal and A. Veillard, *Nouv. J. Chim.*, 1977, **1**, 335; (*c*) M. He and P. Dowd, *J. Am. Chem. Soc.*, 1998, **120**, 1133; (*d*) B. Beatrix, O. Zelder, F. K. Kroll, G. Orlygsson, B. T. Golding and W. Buckel, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2398.

5 C. Lagercrantz, *J. Phys. Chem.*, 1971, **75**, 3466; E. G. Janzen, *Acc. Chem. Res.*, 1971, **4**, 31.

6 L. B. Luo, D. Y. Han, Y. Wu, X. Y. Song and H. L. Chen, *J. Chem. Soc., Perkin Trans. 2*, 1998, 1709.

7 M. L. Bender and M. Komiyama, *Cyclodextrin Chemistry*, Springer, Berlin, 1978; J. Szejtli, *Cyclodextrins and their Inclusion Complexes*, Akademiai Kiado, Budapest, 1982.

8 R. M. Paton and E. T. Kaiser, *J. Am. Chem. Soc.*, 1964, **86**, 639; N. M. Atherton and S. J. Strach, *J. Chem. Soc., Faraday Trans. 1*, 1975, **71**, 357; M. Okazaki and K. Kuwata, *J. Phys. Chem.*, 1984, **88**, 3163; M. Okazaki and K. Kuwata, *J. Phys. Chem.*, 1984, **88**, 4184; J. Martinie, J. Michon and A. Rassat, *J. Am. Chem. Soc.*, 1975, **97**, 1818; J. Michon and A. Rassat, *J. Am. Chem. Soc.*, 1979, **101**, 995.

9 M. Ata, M. Aoyagi, Y. Kubozono and Y. Gondo, *Chem. Lett.*, 1989, 341.

10 K. Kano, K. Mori, B. Uno, M. Goto and T. Kubota, *J. Am. Chem. Soc.*, 1990, **112**, 8645.

11 (*a*) H. L. Chen, Y. Qian, G. J. Chen and W. X. Tang, *Chin. Sci. Bull.*, 1991, **36**, 42; (*b*) H. Yan, H. L. Chen, Y. Qian and W. X. Tang, *J. Inorg. Biochem.*, 1994, **56**, 265; (*c*) Y. Wu, L. B. Luo, D. Y. Han and H. L. Chen, *Chin. Sci. Bull.*, 1998, **43**, 832; (*d*) X. Y. Song, Y. Chen and H. L. Chen, *Chem. J. Chin. Univ.*, 2000, **21**, 169.

12 J. C. Stowell, *J. Org. Chem.*, 1971, **36**, 3055.

13 G. N. Schrauzer and R. J. Windgassen, *J. Am. Chem. Soc.*, 1966, **88**, 3738.

14 B. T. Golding, T. J. Kemp, P. J. Seller and E. Nocchi, *J. Chem. Soc., Dalton Trans.*, 1977, 1266.

15 M. J. Perkins, P. Ward and A. Horsfield, *J. Chem. Soc. B*, 1970, 395; G. Zweifel, J. T. Snow and C. C. Whitney, *J. Am. Chem. Soc.*, 1968, **90**, 7141.

16 T. Sato, S. Kita and T. Otsu, *Makromol. Chem.*, 1979, **180**, 1911; Y. Maeda and K. U. Ingold, *J. Am. Chem. Soc.*, 1979, **101**, 4975; T. L. Hall, M. F. Lappert and P. W. Lednor, *J. Chem. Soc., Dalton Trans.*, 1980, 1448; E. Flesia, *Tetrahedron Lett.*, 1974, 123.

17 Y. Kotake and E. G. Ianzen, *J. Am. Chem. Soc.*, 1989, **111**, 2066; Y. Kotake and E. G. Ianzen, *J. Am. Chem. Soc.*, 1989, **111**, 5138; Y. Kotake and E. G. Ianzen, *J. Am. Chem. Soc.*, 1989, **111**, 7319; Y. Kotake and E. G. Ianzen, *J. Am. Chem. Soc.*, 1992, **114**, 2872; K. Flohr, R. M. Paton and E. T. Kaiser, *J. Am. Chem. Soc.*, 1975, **97**, 1209; Y. Mortozato, T. Nishihara, C. Hirayama and Y. Furuya, *Can. J. Chem.*, 1982, **60**, 1959.

18 F. Cuiban, *Rev. Chim.*, 1987, **38**, 101.

19 P. Dowd, M. Shapiro and K. Kang, *J. Am. Chem. Soc.*, 1975, **97**, 4754; G. Bidlingmaier, H. Flohr, U. M. Kempe, T. Krebs and J. Retey, *Angew. Chem., Int. Ed. Engl.*, 1975, **14**, 822; S. M. Chemaly and J. M. Pratt, *J. Chem. Soc., Chem. Commun.*, 1976, 988; R. Hamilton, T. R. B. Mitchell, E. A. McIlgorm and J. J. Rooney, *J. Chem. Soc., Chem. Commun.*, 1981, 686.

20 M. J. Davies, B. C. Gilbert and R. O. C. Norman, *J. Chem. Soc., Perkin Trans. 2*, 1983, 731.

21 C. Giannotti, G. Merle and C. Fontaine, *J. Organomet. Chem.*, 1975, **91**, 357.

22 C. Lagercrantz and S. Forshult, *Acta Chem. Scand.*, 1969, **23**, 811.