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Thermal behavior of substituted pyridine adducts of porphyrinatocobalt(II) complexes in the solid state

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Abstract

The thermal behavior of Co(TPP)(L), Co(Tp-CH_3PP)(L), and Co(Tp-OCH_3PP)(L) was investigated in the solid state, where TPP, Tp-CH_3PP, and Tp-OCH_3PP represent tetraphenylporphyrin, tetra(*p*-methylphenyl)porphyrin, and tetra(*p*-methoxyphenyl)porphyrin, respectively, and L represents a series of 4-substituted pyridines. Upon heating, these complexes release a pyridine molecule with a structural change from square-pyramidal five-coordination to square-planar four-coordination. The thermal stability (peak temperature of the DSC curves taken as the reaction temperature) was found to be high when the basicity of the bound pyridine is high or the substituent on the pyridine is large in size. The thermal stability is also correlated to the enthalpy change for this reaction. These results were explained by a difference in the Co–pyridine bond strength and by the packing forces for the pyridine in the crystal lattice. Among the three types of porphyrins, the substituent of porphyrin did not affect the thermal stability, probably because of the greater differences in lattice energy.

INTRODUCTION

Reactions of metalloporphyrins with neutral bases such as imidazoles and pyridines have received considerable attention because of their biological fields [1]. The free energy changes for formation of mono-amine adducts in organic solvents

$$\mathrm{MP} + \mathrm{L} \rightarrow \mathrm{MP} \cdot \mathrm{L} \qquad (1)$$

where MP represents square-planar four-coordinated porphyrin complexes, where M is Co(II) or Zn(II), L represents amine ligands, and MP · L represents square-pyramidal five-coordinated complexes, were found to be correlated well with the pK_a values of the amines [2–4], although compli-

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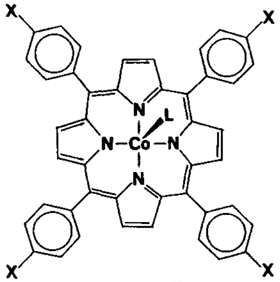
cated solvation phenomena are involved [5–7]. However, for the thermal reaction in the solid state

$$MP \cdot L \rightarrow MP + L \quad (2)$$

the thermal stability of MP · L may be related to the thermodynamic stability of this species in solution. In this report, we examined the solid-state thermal behavior in a series of 4-substituted pyridine adducts of some tetra(*p*-substituted-phenyl)porphyrinatocobalt(II) complexes and explored relationships between the basicity of the pyridines and the thermal stability of the five-coordinated pyridine adducts. Because four-coordinated complexes of simple flat tetraphenylporphyrins are sufficiently thermally stable [8] in the solid state, pyridine-release reactions, eqn. (2), are readily detected by thermal analyses.



Co(Tp-XPP)(L)

EXPERIMENTAL

Materials

Cobalt(II) complexes of *meso*-tetraphenylporphyrin (Co(TPP)), *meso*-tetra(*p*-methoxyphenyl)porphyrin (Co(Tp-OCH_3PP)), and *meso*-tetra(*p*-methylphenyl)porphyrin (Co(Tp-CH_3PP)) were prepared according to the literature [9, 10]. These compounds yielded excellent analytical data (within 0.2% of the calculated values for C, H, and N). Pyridine (py) was distilled from KOH. Other pyridines, 4-cyanopyridine (4-CNpy), 4-chloropyridine (4-Clpy), 4-phenylpyridine (4-phpy), 4-methylpyridine (4-Mepy), 4-*t*-butylpyridine (4-*t*-butpy), 4-aminopyridine (4-NH_2py), and 4-dimethyl-aminopyridine (4-Me_2Npy), were used as supplied without further purification.

Pyridine adducts of the Co(II) porphyrins were obtained as follows. To a solution of 50 mg of Co(TPP) in 30 ml of $CHCl_3$ was added 0.1 ml of pyridine. To the mixture was added dropwise 30 ml of hexane; purple crystals of Co(TPP)(py) were obtained. The solid was filtered off and dried at 50°C under vacuum; yield, 35 mg (63%). Other pyridine adducts were prepared by similar methods.

Measurements

Simultaneous TG and DSC measurements were carried out with a Rigaku Denki standard TG–DSC apparatus. The experimental conditions were a constant flow of N_2 gas at a heating rate of 1.25°C min^{-1} for 10–15 mg of sample. ESR spectra at X-band were obtained using a Jeol JES-FE2GX spectrometer. Visible absorption spectra were recorded on a Hitachi 340 spectrophotometer. Solid-state absorption spectra were obtained in Nujol mulls.

RESULTS AND DISCUSSION

Figure 1 shows an example of the TG and DSC curves of the thermal analyses. In all cases, pyridine is liberated from five-coordinated complexes yielding four-coordinated complexes below 240°C with both an endothermic DSC peak and a weight loss in the TG curve. This reaction was confirmed by solid-state ESR measurements at room temperature, as shown in Fig. 2. After heating, the ESR spectra of the pyridine adducts changed again to the original spectra of the four-coordinated complexes. Tables 1–3 summarize the results of the thermal analyses. Figure 3 plots the reaction temperatures, where T is the peak temperature of the DSC curves, of Co(Tp-OCH_3PP)(L) versus the pK_a value of L. Two factors apparently affect the thermal stability of the pyridine adducts. Firstly, the thermal stability of five-coordinated complexes in which the pK_a of the bound pyridine is small, is relatively low. This can be understood on the basis of the Co–L bond strength as a Lewis acid–base pair and is also in agreement with the relationship that is observed in solution between the thermodynamic stability of the amine adducts and the pK_a of the amines [2–4]. Secondly,

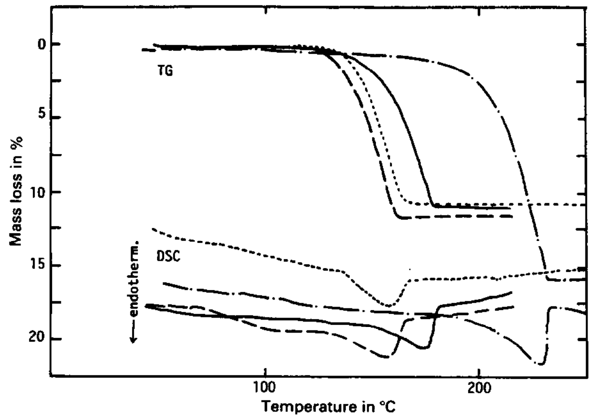


Fig. 1. TG and DSC curves of: ——, Co(Tp-CH_3PP)(4-Mepy); – – –, Co(Tp-OCH_3PP)(4-Clpy); — · — · —, Co(Tp-OCH_3PP)(4-Me_2Npy); and — — —, Co(TPP)(4-Mepy).

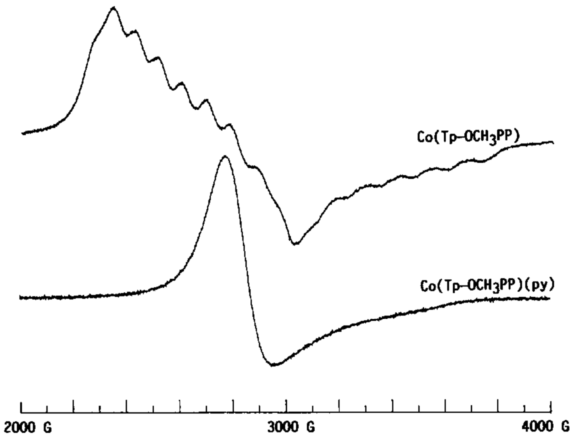


Fig. 2. Polycrystalline ESR spectra of Co(Tp-OCH_3PP) and its pyridine adduct.

TABLE 1

Reaction temperatures and enthalpy changes of Co(TPP)(L)

L	pK_a [a]	T/°C	T_c/°C	ΔH/(kcal mol^{-1}) [b]
4-Clpy	3.83	146.4	122.0	12.6
Py	5.22	139.0	139.0	17.1
4-Phpy	5.35	191.3	139.0	27.8
4-Mepy	5.98	156.2	146.5	19.2
4-*t*-Butpy	5.99	184.3	145.7	26.7
4-NH_2py	9.12	196.0	185.0	17.5
4-Me_2Npy	9.70	235.5	205.2	26.9

[a] Refs. 4 and 11. [b] 1 kcal mol^{-1} = 4.18 kJ mol^{-1}.

TABLE 2

Reaction temperatures and enthalpy changes of Co(Tp-CH_3PP)(L)

L	pK_a	T/°C	T_c/°C	ΔH/(kcal mol^{-1}) [a]
4-Clpy	3.83	142.9	126.7	19.2
Py	5.22	135.7	135.7	18.0
4-Phpy	5.35	171.2	135.7	26.6
4-Mepy	5.98	142.0	135.4	15.4
4-Me_2Npy	9.70	183.6	163.4	27.7

[a] 1 kcal mol^{-1} = 4.18 kJ mol^{-1}.

five-coordinated complexes with a bulk pyridine such as 4-phpy or 4-*t*-butpy show an appreciably higher thermal stability. Similar results were also obtained for the other two porphyrin systems (see Tables 2 and 3).

TABLE 3

Reaction temperatures and enthalpy changes of Co(Tp-OCH_3PP)(L)

L	pK_a	T/°C	T_c/°C	ΔH/(kcal mol^{-1}) [b]
4-CNpy [a]	1.86	124.7	99.9	21.4
4-Clpy	3.83	157.0	123.1	16.6
Py	5.22	147.4	147.4	15.8
4-Phpy	5.35	220.0	147.4	30.7
4-Mepy	5.98	172.4	159.1	22.6
4-*t*-Butpy	5.99	204.8	151.0	25.7
4-NH_2py	9.12	193.6	178.4	24.6
4-Me_2Npy	9.70	227.0	186.1	27.2

[a] Accompanied by some degree of solvent liberation from the crystals. [b] 1 kcal mol^{-1} = 4.18 kJ mol^{-1}.

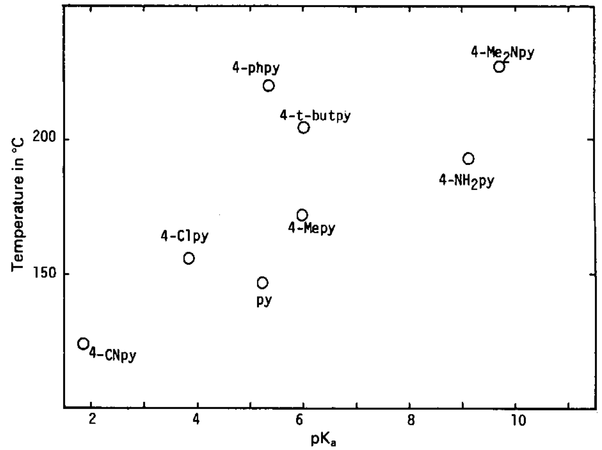


Fig. 3. Plots of reaction temperature T of Co(Tp-OCH_3PP)(L) versus pK_a of pyridines L.

These phenomena can be further understood by introducing the following simple equation

$$T_c = T - C\Delta W$$

where T_c is the corrected reaction temperature, ΔW is the difference in molecular weight between pyridine and substituted pyridines, and C is a constant. The C values were determined to show that the T_c of 4-phpy adduct is equal to that of the corresponding py adduct. Thus, the C values for Co(TPP), Co(Tp-CH_3PP), and Co(Tp-OCH_3PP) were estimated to be 0.69, 0.47, and 0.95°C, respectively. As shown in Fig. 4, excellent linear relationships between T_c and the pK_a of pyridine were obtained in all cases. Thus, a simple correction on reaction temperatures by molecular weights provides a clear correlation between the thermal stability of pyridine adducts and

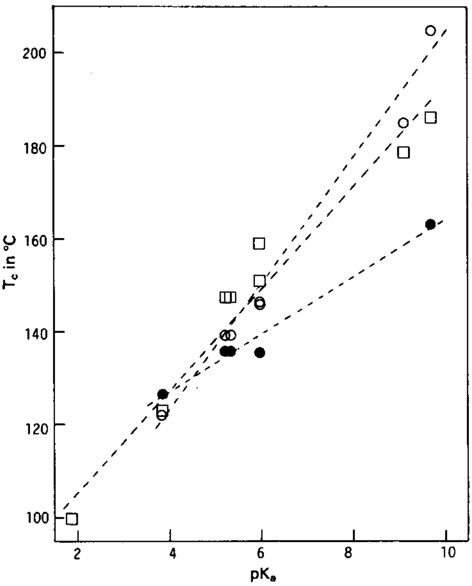


Fig. 4. Relationships between T_c and pK_a of L for: ○, Co(TPP)(L); ●, Co(Tp-CH_3PP)(L); and □, Co(Tp-OCH_3PP)(L).

pyridine basicity. Because the *C* values in the correction term must be related to a solid-specific force such as lattice energy, pyridine liberation from Co(Tp-OCH_3PP), with a large *C* value, may be most affected by the solid-specific force among the three porphyrin systems examined. This is supported by the visible absorption spectral data. In $CHCl_3$ solution, the absorption spectra of the three types of four-coordinated complexes and their pyridine adducts are similar to each other and their two absorption maxima fall in the range between 411 and 414 nm (soret) and between 527 and 530 nm (not shown). In the solid state, these absorption maxima shift to longer wavelengths, as listed in Table 4. These deviations are associated with the

TABLE 4

Absorption maxima (nm) of porphyrin complexes in the solid state

L	Co(TPP)	Co(Tp-CH_3PP)	Co(Tp-OCH_3PP)
	425, 535	425, 535	430, 540
4-CNpy		422, 538	430, 538
4-Clpy	424, 540	424, 540	430, 540
Py	422, 540	424, 540	430, 540
4-Phpy	420, 540	420, 538	425, 540
4-Mepy	420, 540	422, 540	425, 540
4-*t*-Butpy	420, 558		428, 538
4-NH_2py	424, 540		430, 542
4-Me_2Npy	420(sh), 440, 540	423, 544	435, 540

solid-specific effect stated above. The soret bands of Co(Tp-OCH_3PP)(L) in the solid state appear at a longer wavelength, by about 5 nm, than those of Co(TPP)(L) and Co(Tp-CH_3PP)(L). This result may reasonably be related to the fact that the *C* value of Co(Tp-OCH_3PP) is larger than those of the other porphyrins.

For the enthalpy changes on pyridine liberation, two similar relationships with respect to the pK_a values of pyridines can be recognized in all cases. Firstly, the liberation of pyridines with high basicity requires a relatively high energy (ΔH) to cleave the strong Co–L bond. Secondly, pyridines with a bulky substituent are released with a larger ΔH value compared to unsubstituted pyridine liberation. It is most likely that the excess energy ($\Delta\Delta H$) in terms of the presence of a bulk substituent such as C_6H_5- or $(CH_3)_3C-$ derives from the liberation energy of the substituent from the crystal lattice. This term will depend on molecular weight but is independent of the Co–L bond strength, if the crystal lattice is not much changed upon pyridine liberation.

The substituent effects of porphyrin on the thermodynamic stability of amine adducts of Co(II) and Zn(II) TPP derivatives in solution have been reported [12, 13]; the presence of electron-withdrawing substituents at the para-position on phenyl groups of TPP enhances the thermodynamic stability of the amine adducts by decreasing the electron density on the central metal ion, leading to a strengthening of the metal–amine bond. In this case, however, no correlation between the thermal stability of the pyridine adducts and the substituents of the porphyrins is apparent. For all pyridines, the *T* values of Co(Tp-CH_3PP) are lower than those of the corresponding pyridine adducts of Co(TPP) and Co(Tp-OCH_3PP). This may be due to the greater influences of solid-state factors such as the differences in crystal packing forces which predominate over the substituent effects of porphyrin.

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