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Metal-metal bonds extended over a porphyrin ring

III *. Syntheses and spectral studies of new metal–metal bonded indium porphyrin complexes, (TBPP)In–ML and (5FP)In–ML

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Abstract

Two new series of metal–metal bonded indium porphyrin complexes, (TBPP)In–ML and (5FP)In–ML, where TBPP is the dianion of 5,10,15,20-tetrakis (3,5-di-t-butylphenyl)porphyrin and 5FP is the dianion of 5,10,15,20-tetrakis(2,3,4,5,6-pentafluorophenyl)porphyrin, ML is $Mn(CO)_5$, $Mo(CO)_3Cp$, and $Co(CO)_4$, have been synthesized in addition to (OEP)In–ML and (TPP)In–ML. These new metal–metal bonded porphyrin complexes have shown higher solubilities to organic solvents or higher photochemical stabilities as compared with (OEP)In–ML and/or (TPP)In–ML. (P)In–$Co(CO)_4$ complexes where P denotes all of these porphyrin ligands have been obtained in almost quantitative yield by the reaction of (P)In–Cl with $LiCo_3(CO)_{10}$. These porphyrin complexes have shown typical UV-vis spectra to the hyper class. Analysis of the absorption spectra has revealed an anomalous character of (5FP)In–ML complexes. ^{17}O and ^{13}C NMR chemical shifts for CO ligands in (P)In–ML complexes have exhibited only small changes with the change of the porphyrin ligand for the same ML. IR data of (P)In–ML complexes in the $\nu(CO)$ region have clearly shown higher frequency shifts in inverse proportion to σ-donor ability of these four porphyrin ligands.

Introduction

Recently, a significant number of papers describing the synthesis and characterization of heteronuclear metal–metal bonded porphyrin complexes have been

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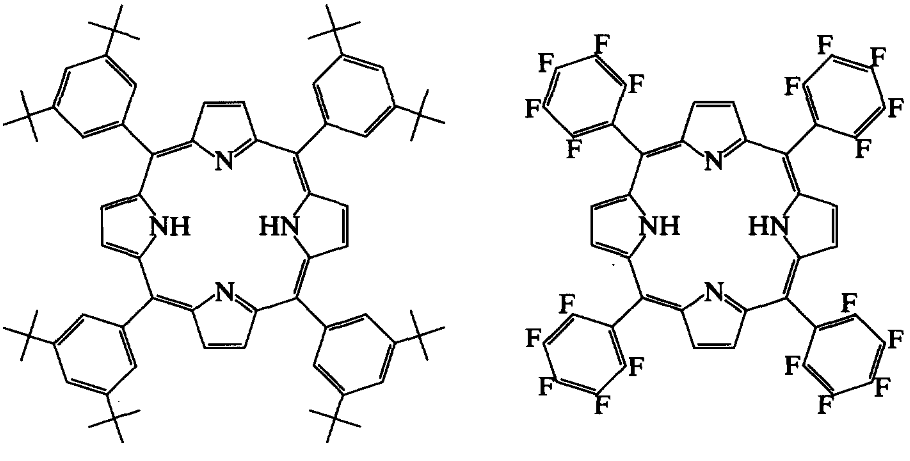
reported. These porphyrin complexes are classified into two types depending on the metal–metal bond included; that is, (1) carbenoid-type metal–metal bonded porphyrins with donor–acceptor character for the metal–metal bond such as (TPP)Sn–Mn$(CO)_4$HgMn$(CO)_5$ [2], (TPP)Sn–Co$(CO)_3$HgCo$(CO)_4$ [3], and (P)M-Fe$(CO)_4$ [4] (P = TPP [5*], OEP [6*]; M = Ge, Sn), and (2) typical σ-type metal–metal bonded porphyrins such as (P)In–Rh(P) [7], (P)In–ML [3,8,9] and (P)Tl–ML [10] where P is a dianion of the porphyrin ligand and ML is a metal carbonyl moiety. In these metal–metal bonded porphyrin complexes, only a few kinds of porphyrin ligands such as TPP or OEP have been employed, although the character of the metal–metal bond is expected to be significantly affected by the electronic structure or the steric environment of the porphyrin ligand. Thus, it is of great interest to develop the synthesis of heteronuclear metal–metal bonded porphyrins other than TPP and/or OEP. It is our main purpose to synthesize new metal–metal bonded indium porphyrin complexes, (P)In–ML, by use of TPP derivatives.

Various spectroscopic methods, such as UV-vis, IR, and NMR have been adopted in the studies of metal–metal bonded porphyrin complexes. Although ^{17}O NMR is a very useful method to obtain electronic and structural information about the metal carbonyl moiety [11,12], there has been no report on the ^{17}O NMR study of metal–metal bonded porphyrin complexes to our knowledge. Major difficulties in the measurements of ^{17}O NMR spectra are two-fold; low natural abundance (0.037%) of the ^{17}O nucleus and low solubility of metal–metal bonded porphyrin complexes so far synthesized. These problems should be overcome by preparing more lipophilic metal–metal bonded porphyrins. Therefore, we have employed 5,10,15,20-tetrakis(3,5-di-t-butylphenyl)porphyrin ($TBPPH_2$, Fig. 1) which is quite a lipophilic porphyrin [13]; solubility of $TBPPH_2$ in pentane is approximately 390 times greater than that of $TPPH_2$ [14]. Thus, (TBPP)In–ML complexes are



$TBPPH_2$ $5FPH_2$

Fig. 1. Structures of $TBPPH_2$ and $5FPH_2$.

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* Reference number with asterisk indicates a note in the list of references.

expected to show good solubility in hydrocarbon solvents as compared with (TPP)In–ML or (OEP)In–ML complexes and to afford good ^{17}O NMR data; this expectation composes the second purpose of the present study.

The indium-metal bond is susceptible to UV irradiation. As (TPP)In–ML complexes are a little more resisting to photochemical cleavage of the In–M bond than (OEP)In–ML complexes, it seems feasible that the effective protection around the porphyrin metal center enhances the photostability of the In–M bond. One method to attain steric protection around the porphyrin center is to introduce t-butyl groups at the metal position of the meso phenyl moieties. More effective protection is possible by substituting fluorine atoms for all the hydrogen atoms of the meso phenyl groups. Thus, 5,10,15,20-tetrakis(2,3,4,5,6-pentafluorophenyl) porphyrin ($5FPH_2$, Fig. 1) has been employed as a protecting porphyrin ligand. The third purpose of the present study is to examine the steric effect of the porphyrin ligand on the stability of the indium-metal bond.

Here we report the synthesis and spectral studies of metal–metal bonded new indium porphyrins, and the assay how our aim is achieved by changing the porphyrin ligand.

Experimental

All solvents were purified by standard means. Porphyrin free bases, $TPPH_2$, $OEPH_2$, $TBPPH_2$, and $5FPH_2$ were synthesized by Rothemund condensation or literature methods [15]. The indium insertion reaction was carried out by a modified literature method [16]. All metal carbonyls, $Mn_2(CO)_{10}$, $Co_2(CO)_8$, and $[Mo(CO)_3Cp]_2$ were purchased from Strem Chemicals, and were purified by sublimation. Synthetic procedures except column chromatography were carried out under an Ar atmosphere. ^1H NMR spectra were recorded with a Hitachi Perkin–Elmer R-24B spectrometer (60 MHz). IR spectra were recorded on a Jasco 701G spectrometer. UV-vis spectra were measured by use of a Hitachi 220A spectrophotometer.

Synthesis of (P)In–Mn(CO)$_5$ and (P)In–Mo(CO)$_3$Cp

These complexes were synthesized by reaction of (P)InCl with $Na^+[ML]^-$ ($ML = Mn(CO)_5$, $Mo(CO)_3Cp$) in THF as shown in eq. 1 [3,9]:

$$(P)InCl + Na^+[ML]^- \rightarrow (P)In{-}ML + NaCl \qquad (1)$$

A typical procedure is as follows: A THF solution of $Mn_2(CO)_{10}$ (80 mg, 0.20 mmol in 20 cm^3 of THF) was stirred over 1% Na–Hg (65 g) for 1 h. The resulting grayish-green supernatant was transferred to a 200 cm^3 three-necked flask and to this was added a 100 cm^3 THF solution of (TBPP)InCl (403 mg, 0.33 mmol). The color of the mixture immediately changed from red to green. After additional stirring at room temperature for 2 h, THF was distilled off at reduced pressure. The crude material thus obtained was purified by silica-gel (Wako gel C-200) column chromatography using benzene as an eluent. Yield 364 mg, 0.265 mmol (80%). Synthesis of the metal–metal bonded porphyrin was confirmed by an elemental analysis, UV-vis, ^1H NMR (60 MHz, C_6D_6), and IR spectra [17*]. Other metal–metal bonded porphyrin complexes were synthesized by similar procedures [18*].

Synthesis of (TBPP)In–Co(CO)$_4$ (method 1)

A methanol solution (30 cm^3) of $Co_2(CO)_8$ (200 mg, 0.59 mmol) was refluxed for 1 h. To the resulting methanol solution of 0.59 mmol of $[Co(CO)_4]^-$, a 0.33 mmol amount of (TBPP)InCl in 100 cm^3 THF was added and the mixture was stirred at ambient temperature for 2 h. Then solvents were vacuum-stripped and the residue was dissolved in a minimum amount of benzene. The benzene solution was loaded on a silica-gel (Wako gel C-200) column and the green product was eluted with benzene. Drying the effluent gave 250 mg (56%) of (TBPP)In–Co(CO)$_4$; synthesis of this product was confirmed by UV-vis, ^{1}H-NMR, and IR spectra.

Synthesis of (TBPP)In–Co(CO)$_4$ (method 2)

The title product was synthesized by reacting (TBPP)InCl with $Li^+[Co_3(CO)_{10}]^-$ [19]. Typical procedures are as follows: A 100 cm^3 ether solution of $Co_2(CO)_8$ (400 mg, 1.17 mmol) was cooled to 10°C. To this was added 500 mg of small lithium globules and the mixture was stirred until the gas evolution ceased. The resulting deep red solution was dropped into a THF solution (50 cm^3) of (TBPP)InCl (400 mg, 0.33 mmol) by use of a syringe and the mixture was stirred at room temperature for 2 h. The solvents were distilled off at reduced pressure from the resulting green solution. The residue was redissolved in a minimum amount of benzene and was loaded on a silica-gel column (Wako gel C-200) using benzene as an eluent. The green band was collected. Yield 430 mg (97%). Synthesis of this complex was confirmed by an elemental analysis, ^{1}H NMR, IR, and UV-vis spectra [20*]. Other (P)In–Co(CO)$_4$ complexes were synthesized by similar procedures, and syntheses of these complexes were confirmed by UV-vis, ^{1}H NMR (60 MHz, C_6D_6) [21*], and IR spectra.

^{17}O NMR and ^{13}C NMR measurements

Sample solutions for NMR measurements were prepared by a vacuum-line technique; solvents were completely deaerated by freeze-thaw cycles, distilled into a 10 mm o.d. NMR tube, and the tube was sealed off under vacuum. ^{17}O NMR and ^{13}C NMR spectra were recorded on a Varian XL-200 spectrometer for saturated solutions containing C_6D_6 as a lock solvent at 23°C with a Fourier transform mode for the naturally abundant level. ^{17}O NMR spectra were measured with 90° pulse, 0.04 s acquisition time, and 1 080 000 scans. ^{13}C NMR spectra were measured with 45° pulse, 0.8 s acquisition time, and 1600 scans. Chemical shifts were measured in parts per million with reference to $H_2{}^{17}O$ (^{17}O) or TMS (^{13}C).

Results and discussion

Synthesis and properties of metal–metal bonded porphyrins

Metal–metal bonded new indium porphyrins have been synthesized by the reaction of (P)InCl complexes with $Na^+[ML]^-$ except for (5FP)In–Co(CO)$_4$ and the yields are summarized in Table 1. The yield of (TBPP)In–Co(CO)$_4$ is low compared with those of other TBPP complexes. A similar result had been provided by Guilard *et al.* [9]; the yield of (TPP)In–Co(CO)$_4$ reported by them was about one-third of those of (TPP)In–Mo(CO)$_3$Cp and (TPP)In–Mn(CO)$_5$. They interpreted the result in terms of the nucleophilic power of the anions [9,22]. Therefore, we have examined a new synthetic approach to (P)In–Co(CO)$_4$ complexes, that is,

Table 1

Percent yields for (TBPP)In–ML and (5FP)In–ML complexes

	$Mn(CO)_5$	$Mo(CO)_3Cp$	$Co(CO)_4$	
			Method 1	Method 2
(TBPP)In–ML	80	81	56	97
(5FP)In–ML	90	96	–	99

the use of $Li^+[Co_3(CO)_{10}]^-$ instead of $[Co(CO)_4]^-$ [19]. When the diethyl ether solution containing $Li^+[Co_3(CO)_{10}]^-$ is added to the THF solution of (P)InCl at ambient temperature, the desired (P)In–$Co(CO)_4$ complex is obtained in almost quantitative yield (Table 1). This synthetic procedure is quite useful for the synthesis of (P)In–$Co(CO)_4$, although the reaction mechanism of the formation of (P)In–$Co(CO)_4$ is not yet clear. Presumably (P)In–$OCCo_3(CO)_9$ is formed at first and then this cluster is degraded to (P)In–$Co(CO)_4$. The detailed reaction mechanism is now under investigation.

The axial metal carbonyl moiety, ML, in (P)In–ML is immediately exchanged by chloride in dichloromethane or chloroform solution unless the solution is stored in the dark. Figure 2 shows the spectral change of the chloroform solution of (TBPP)In–$Mn(CO)_5$ with 500 nm light irradiation. Two bands at 389 and 457 nm in the Soret region due to the (TBPP)In–$Mn(CO)_5$ are gradually faded and the new Soret peak at 432 nm due to (TBPP)InCl grows. The observed exchange rate of the axial ML moiety in $CHCl_3$ solution is in the order OEP > TPP > TBPP > 5FP. The present series of metal–metal bonded porphyrin derivatives display color changes from dark green to wine-red even in benzene solutions by sunlight irradiation (Fig. 3). This color change should reflect the cleavage of the metal–metal bond involved, although the products from this color change process in benzene have not yet been well characterized. The observed rate of the aforementioned color change decreases in the order OEP > TPP > TBPP > 5FP and this order is completely in accord with that for the cleavage of the metal–metal bond by chloroform. From these two experiments, it has been concluded that the kinetic stability of the metal–metal bond is in the order (5FP)In–ML > (TBPP)In–ML > (TPP)In–ML > (OEP)In–ML. Both faces of the porphyrin plane for TPP, TBPP, and 5FP possess a hydrophobic pocket on each side of the porphyrin plane that is formed by meso-phenyl moieties, although OEP has an open pocket on each side of the plane (Fig. 4). Therefore, the steric protection of the porphyrin ligand is supposed to be in the order of OEP < TPP < TBPP < 5FP based on the CPK model. This order is just the same as the order of the metal–metal bond stability mentioned above.

To assess our second purpose described in the introduction, the solubilities in organic solvents especially in hydrocarbons (such as n-hexane) have been investigated for the present (four) series of porphyrin derivatives; the solubilities of (TBPP)In–ML or (5FP)In–ML complexes are higher than those of (TPP)In–ML or (OEP)In–ML analogues and (TBPP)In–ML complexes are quite soluble in n-hexane as was expected. Since (TBPP)In–ML and (5FP)In–ML complexes have high stabilities and solubilities as compared with (TPP)In–ML and (OEP)In–ML, these complexes are easily purified by silica gel column chromatography by use of

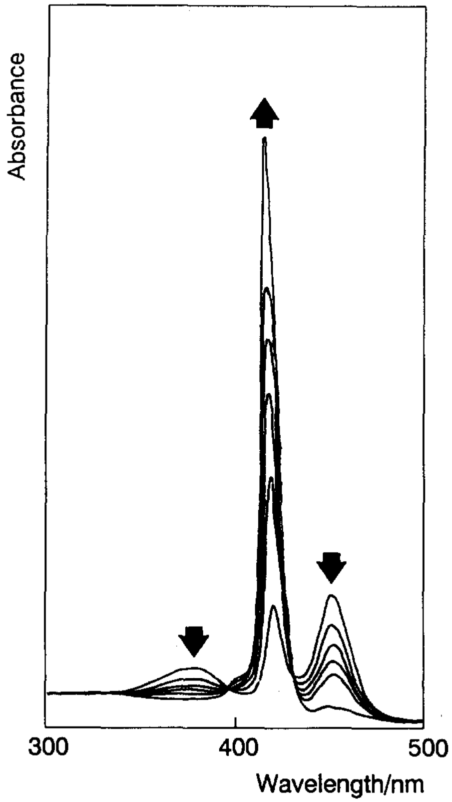

Fig. 2. Spectral changes of (TBPP)In–Mn(CO)$_5$ complex in chloroform with 500 nm light irradiation. Each spectrum was recorded at 3 min, 30 min, 60 min, 90 min, 120 min, or 24 h.

benzene as an eluent at ambient temperature. However purification of (OEP)In–ML by column chromatography is quite difficult because of their instability under the same conditions.

UV-vis spectra of metal–metal bonded porphyrins

The UV-vis spectral data of each complex in benzene are summarized in Table 2. The absorption spectra of (P)InCl complexes are classified as "normal" porphyrin spectra [23]. In contrast, the metal–metal bonded porphyrins show electronic absorption spectra belonging to the so-called "hyper" class [23]. The hyper porphyrin shows a prominent extra absorption band ($\epsilon > 1000\ M^{-1}\ \mathrm{cm}^{-1}$) in the near-UV region. For the series of (P)In–ML, the Soret band splits into two bands (labeled band I and II), which appear in the range 370–470 nm. The Soret band (band II) involves a $\pi \rightarrow \pi^*$ electronic transition and shows a red shift (20–45 nm) when the chloride ion in (P)InCl is replaced with the ML moiety. The extra absorption in the near-UV region (band I) is a charge-transfer band from the indium metal to the porphyrin ring, $a_{2u}(5P_z) \rightarrow e_g(\pi^*)$ [9], to which a significant contribution of the charge transfer from the metal–metal bond is expected; charge density on the indium atom is increased by the formation of the indium–metal bond, and this causes the charge transfer.

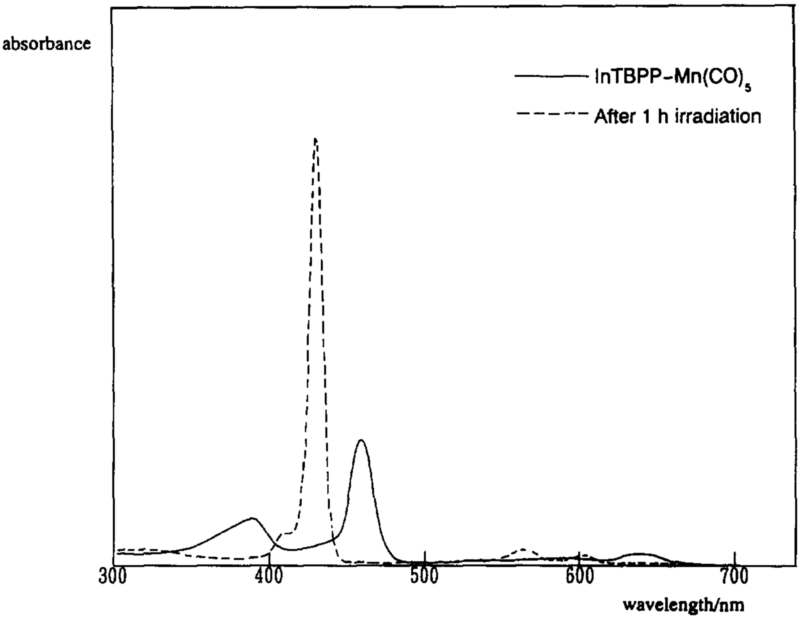

Fig. 3. Spectral change of (TBPP)In–Mn$(CO)_5$ complex in benzene with 1 h sunlight irradiation.

The ratios of molar absorption between band II and I (ϵ_{II}/ϵ_I) are also listed in Table 2. The ϵ_{II}/ϵ_I value can be related to the electron-donating ability of the axial ligand, ML, or of the porphyrin ring [9]; Kadish et al. reported that the complexes with electron-donating R groups had a smaller ϵ_{II}/ϵ_I ratio for σ-bonded In–alkyl or In–aryl porphyrins, (P)In–R [24]. The order of ϵ_{II}/ϵ_I ratios in (OEP)In–ML and (TPP)In–ML complexes is $Co(CO)_4 > Mo(CO)_3Cp > Mn(CO)_5$. This order is reversed for the sequence of the electron donating ability of ML, $Co(CO)_4 < Mo(CO)_3Cp < Mn(CO)_5$ [25]. The order of ϵ_{II}/ϵ_I for (TBPP)In–ML or (5FP)In–ML is rather different from this order, that is, $Co(CO)_4 > Mn(CO)_5 = Mo(CO)_3Cp$ for (TBPP)In–ML and $Co(CO)_4 > Mn(CO)_5 > Mo(CO)_3Cp$ for (5FP)In–ML. When the hydrogen atoms in *meso*-phenyl groups are replaced with t-butyl groups (TBPP) or fluorines (5FP), steric crowding around the porphyrin plane occurs. Since the $[Mo(CO)_3Cp]^-$anion is a sterically bulky ligand compared to the other two anions ($[Co(CO)_4]^-$ and $[Mn(CO)_5]^-$), a steric hindrance between porphyrin and axial ligated $Mo(CO)_3Cp$ should bring the indium–metal bond elongation or the indium metal displacement from the porphyrin plane in the

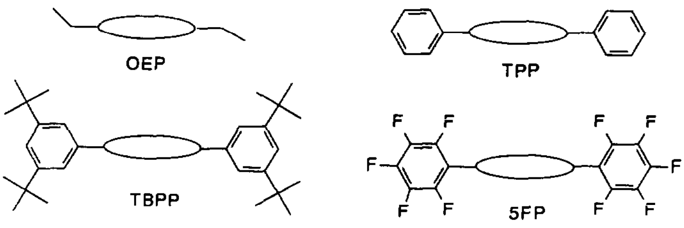

Fig. 4. Steric environments of four porphyrin ligands.

Table 2

UV-vis data of (P)In–ML complexes in benzene

Porphyrin	ML	λ_{max} (nm)					$\epsilon_{II}/\epsilon_{I}$
		Soret region		Q-band			
		Band I	Band II				
(TPP)In	Cl	–	427	560	601		–
	$Mn(CO)_5$	392	460	548	587	633	2.0
	$Mo(CO)_3Cp$	383	457	554	588	634	2.4
	$Co(CO)_4$	372	448	578	621		6.1
(OEP)In	Cl	–	411	539	578		–
	$Mn(CO)_5$	380	452	560	594		0.61
	$Mo(CO)_3Cp$	385	452	567	595		0.93
	$Co(CO)_4$	372	437	532	586		1.7
(TBPP)In	Cl	–	432	566	606		–
	$Mn(CO)_5$	389	457	550	592	638	2.6
	$Mo(CO)_3Cp$	388	457	550	592	638	2.6
	$Co(CO)_4$	373	452	578	621		6.1
(5FP)In	Cl	–	423	554	592		–
	$Mn(CO)_5$	394	466	545	583	630	0.57
	$Mo(CO)_3Cp$	394	463	557	586		0.50
	$Co(CO)_4$	380	454	572			1.6

order of (5FP)In–$Mo(CO)_3Cp$ > (TBPP)In–$Mo(CO)_3Cp$. Thus, the nucleophilic power of the $[Mo(CO)_3Cp]^-$ anion is weakened by these In–M bond elongations or displacements, and the $\epsilon_{II}/\epsilon_{I}$ value of (P)In–$Mo(CO)_3Cp$ is lowered in these two metal–metal bonded complexes.

The classification of the electron-donating ability of the porphyrin ligand is estimated as follows; replacement of pyrrole β-H in the porphyrin ring by electron donating ethyl groups increase the σ-donor character of the porphyrin ligand. Substitution with highly electron-withdrawing fluorine atoms at the *meso*-phenyl moieties decreases the σ-donor property. Although TBPP possesses eight tertiary butyl groups which are quite electron donating substituents, these tertiary butyl groups replace metal hydrogens in *meso*-phenyl moieties of TPP. For this replacement at the *meta* positions, the resonance effect by substituents on the porphyrin ring is not significant as compared with the *ortho*- and/or *para*-replacements in *meso*-phenyl groups. Thus, the difference in electron donating character between TBPP and TPP is small. In this way, the σ-donor properties of the porphyrin ligands should be summarized in the order, OEP > TBPP ≈ TPP > 5FP. However, σ-donor properties of the porphyrin ligand estimated from the $\epsilon_{II}/\epsilon_{I}$ ratio are in the order OEP ≈ 5FP > TBPP ≈ TPP. The classification of TBPP and TPP in the same order based on the $\epsilon_{II}/\epsilon_{I}$ ratio is consistent with the discussion on the σ-electron-donating abilities of these two porphyrin ligands advanced above. However, the interpretation that the σ-donor properties of 5FP and OEP is in the same order based on the $\epsilon_{II}/\epsilon_{I}$ ratio is intractable. We speculate that the In–M bond in the (5FP)In–ML complex is elongated by steric congestion and the charge transfer from the metal–metal bond is reduced, or the indium metal is displaced from the

Table 3

Data from ^{17}O NMR and ^{13}C NMR of (P)In–ML complexes and selected mixed metal carbonyl clusters in benzene

Complex	δ (ppm)		Reference
	^{17}O	^{13}C	
(TPP)In–Mn(CO)$_5$	377	–	This work
–Mo(CO)$_3$Cp	396 (*trans*), 382 (*cis*)	–	This work
–Co(CO)$_4$	349	–	This work
(OEP)In–Mn(CO)$_5$	–	–	
–Mo(CO)$_3$Cp	–	–	
–Co(CO)$_4$	347	–	This work
(TBPP)In–Mn(CO)$_5$	378	213	This work
–Mo(CO)$_3$Cp	397 (*trans*), 382 (*cis*)	221	This work
–Co(CO)$_4$	348	197	This work
(5FP)In–Mn(CO)$_5$	379	211	This work
–Mo(CO)$_3$Cp	400 (*trans*), 386 (*cis*)	221	This work
–Co(CO)$_4$	351	197	This work
Me$_2$Sn[Mn(CO)$_5$]$_2$	382 (eq), 366 (ax)	–	12
Mn$_2$Sn[Mo(CO)$_3$Cp]$_2$	410 (*trans*), 393 (*cis*)	–	12
Me$_2$Sn[Co(CO)$_4$]$_2$	360	–	12

porphyrin plane by steric congestion and the charge transfer from the indium metal to porphyrin ligand is reduced.

NMR and infrared spectra

A low natural abundance of the ^{17}O nucleus (0.037%) hinders the measurement of ^{17}O NMR. In addition, low solubilities of (OEP)In–ML and (TPP)In–ML complexes make it more difficult to obtain good data from ^{17}O NMR spectra. However, we have overcome these problems by employing highly lipophilic (P)In–ML complexes, such as (TBPP)In–ML and (5FP)In–ML. The chemical shifts of ^{17}O NMR measurements are summarized in Table 3. The limited solubilities of (OEP)In–Mn(CO)$_5$ and (OEP)In–Mo(CO)$_3$Cp have prevented good ^{17}O NMR spectra being obtained. Data from the ^{13}C NMR measurements of (TBPP)In–ML and (5FP)In–ML complexes are also listed in Table 3. The structures of ML in these (P)In–ML complexes are illustrated in Fig. 5. The Mn(CO)$_5$ unit has four equatorial and one axial carbonyl. The Co(CO)$_4$ unit has three equatorial and one axial carbonyl. The Mo(CO)$_3$Cp unit has two carbonyl groups (cis and trans). The spectral data of ^{17}O NMR of some mixed metal carbonyl clusters in our previous work [12] are also listed in Table 3. The mixed metal cluster containing molybdenum cyclopentadienyl, Me$_2$Sn[Mo(CO)$_3$Cp]$_2$, has two peaks with 2:1 relative intensity. The Mo(CO)$_3$Cp unit of metal–metal bonded porphyrin also has two peaks with 2:1 intensity ratio. The cobalt carbonyl unit of the mixed metal carbonyl cluster, Me$_2$Sn[Co(CO)$_4$]$_2$, or (P)In–Co(CO)$_4$ shows unresolved ^{17}O NMR spectra. Although the mixed metal cluster, Me$_2$Sn[Mn(CO)$_5$]$_2$, shows two peaks with relative intensity of 4:1, (P)In–Mn(CO)$_5$ has only one peak of carbonyl resonance, suggesting the fluxional behavior of carbonyl ligands. Low temperature

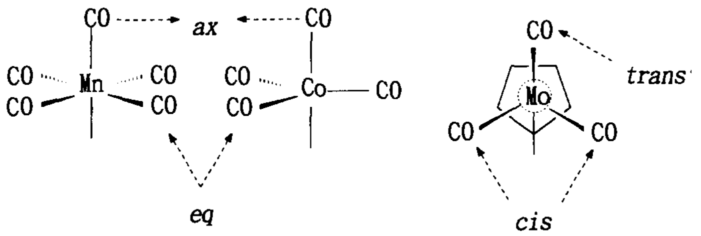

Fig. 5. Structures of metal carbonyl moieties in (P)In–ML complexes.

^{17}O NMR measurements have been carried out. However the solubilities of the metal–metal bonded porphyrins have been extremely lowered by cooling, and good spectra have not yet been obtained. This issue must wait for future experiments. ^{13}C NMR data of (P)In–Mo(CO)$_3$Cp show a difference from the ^{17}O NMR data in that (P)In–Mo(CO)$_3$Cp complexes, where P = TBPP, TPP, and 5FP, have only one broad peak in the carbonyl region. As molybdenum has the large nuclear quadrupole moment, the interaction with this large quadrupole moment should cause the broadening of the peaks as was reported previously [11b].

Good correlation between the ^{13}C and ^{17}O NMR chemical shifts is clarified in Fig. 6 for (TBPP)In–ML and (5FP)In–ML. A similar correlation between ^{13}C and ^{17}O chemical shifts has been reported by Box and Gray for a series of (TPP)Fe^{II}(CO)L complexes [26]. They have explained the change of ^{13}C and ^{17}O chemical shifts in terms of the Buchner and Schenk interpretation [27] and shown that the carbonyl ^{17}O NMR chemical shift is more sensitive to variations in the electron-donor abilities of other ligands than is the carbonyl ^{13}C NMR chemical shift. In the present series of porphyrin derivatives, however, changes of ^{17}O NMR

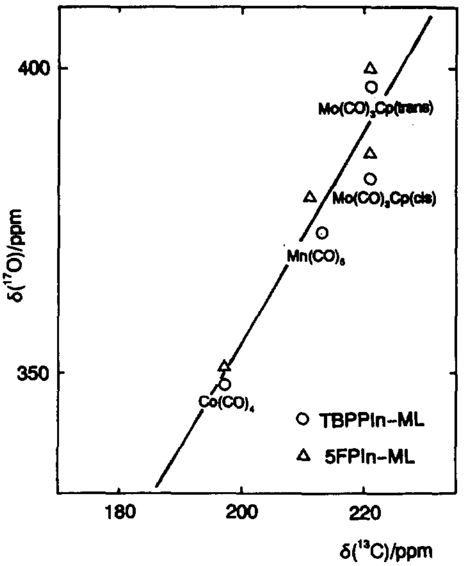

Fig. 6. Correlation between ^{13}C and ^{17}O NMR chemical shifts of (TBPP)In–ML and (5FP)In–ML complexes as the ML group is varied.

Table 4

IR data (benzene solution) in CO stretch region of (P)In–ML complexes

Porphyrin	ML	ν(CO) (cm^{-1})		
(TPP)In	$Mn(CO)_5$	2080	1965	
	$Mo(CO)_3Cp$	1984	1909	1886
	$Co(CO)_4$	2070	1999	1970
(OEP)In	$Mn(CO)_5$	2070	1960	
	$Mo(CO)_3Cp$	1975	1890	1870
	$Co(CO)_4$	2071	2000	1964
(TBPP)In	$Mn(CO)_5$	2079	1972	
	$Mo(CO)_3Cp$	1984	1909	1886
	$Co(CO)_4$	2070	1999	1970
(5FP)In	$Mn(CO)_5$	2089	1981	
	$Mo(CO)_3Cp$	1998	1928	1902
	$Co(CO)_4$	2082	2012	1975

chemical shifts and those of ^{13}C NMR chemical shifts with the change of the porphyrin ligand are almost in the same range and such sensitivity difference has not yet been detected; substitution occurs on the phenyl groups which are far from the metal carbonyl moiety compared with those of (TPP)Fe^{II}(CO)L.

On the contrary, carbonyl stretching frequencies in the IR measurements are considerably sensitive to the change of porphyrin ligand as is shown in Table 4 and are in the order (5FP)In–ML > (TBPP)In–ML = (TPP)In–ML > (OEP)In–ML. As the carbonyl stretching frequency shifts to higher energy for simple metal carbonyl derivatives, $LM(CO)_n$, when L is exchanged with an electron withdrawing ligand L′ [28], the aforementioned order of the higher frequency shifts can be best interpreted in the same way, that is, 5FP is the most electron withdrawing porphyrin ligand and OEP is the best electron donating porphyrin. Thus, the electron donor character of the porphyrin ligand measured in terms of the carbonyl stretching frequencies is in the order OEP > TBPP = TPP > 5FP. This order is in good accordance with the order of the porphyrin ligand electron donating property discussed in the section on UV-vis spectra, although this order is not consistent with that based on the ϵ_{II}/ϵ_I ratio. It seems necessary to scrutinize the origin of the extra absorption (band I) in the metal–metal bonded porphyrins before we can gain any clear insight into this issue.

The spectral pattern of each complex is in good agreement with that of Guilard *et al.* [9] and this coincidence provides strong support to the synthesis of each new porphyrin derivative. All the manganese carbonyl derivatives exhibit two ν(CO) peaks instead of the three predicted bands, $2A_1 + E$ for C_{4v} local symmetry around the manganese atom, probably because the broad band at lower frequencies embraces two of these vibrations ($A_1 + E$). The surroundings about the manganese carbonyl moiety which is engendered by porphyrin substituents should have some connection with this coincidence, because simple manganese carbonyl derivatives of the type $LMn(CO)_5$ show three ν(CO) patterns [25].

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17 Anal. Found: C, 71.33; H, 7.15; N, 4.21. $InMnC_{81}H_{92}N_4O_5 \cdot 1/2C_6H_{14}$ calc.: C, 71.33; H, 7.05; N, 3.96%. ^1H NMR (60 MHz, C_6D_6): 9.17 (s, 8H, pyrrole-β(H)), 8.40 (s, 4H, *o*-phenyl), 8.12 (s, 4H, *o*-phenyl), 7.89 (s, 4H, *p*-phenyl), 1.52 (s, 36H, t-butyl), 1.48 (s, 36H, t-butyl). IR (C_6H_6 solution): ν(CO) 2079, 1972 cm^{-1}. UV-vis (C_6H_6): 389, 457, 550, 592, 638 nm.

18 ^1H NMR (TBPP)In–Mo$(CO)_3$Cp: 9.12 (s, 8H, pyrrole-β(H)), 8.43 (s, 4H, *o*-phenyl), 8.10 (s, 4H, *o*-phenyl), 7.86 (s, 4H, *p*-phenyl), 2.69 (s, 5H, Cp), 1.48 (s, 36H, t-butyl), 1.45 (s, 36H, t-butyl). (5FP)In–Mn$(CO)_5$: 8.98 (s, 8H, pyrrole-β(H)). (5FP)In–Mo$(CO)_3$Cp: 8.88 (s, 8H, pyrrole-β(H)), 2.85 (s, 5H, Cp).

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