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Carbon Dioxide Insertion into the Methyl-Indium σ Bond of Methylindium(III) Porphyrins. Molecular Stereochemistry of (Acetato)(2,3,7,8,12,13,17,18-octaethylporphyrinato)indium(III)

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Carbon dioxide inserts into the indium–carbon σ bond of methylindium(III) porphyrins upon irradiation by visible light in dry benzene/pyridine media, leading to stable acetato complexes. The same products have been prepared by action of acetic acid on either the alkyl(aryl)indium(III) porphyrins or the aquohydroxoindium(III) porphyrins. The crystal structure of the title compound has been determined by X-ray diffraction methods: $(OEP)InCO_2CH_3{\cdot}2CHCl_3$, $InO_2N_4C_{38}H_{47}{\cdot}2CHCl_3$; $M_r = 945$; triclinic, $P\bar{1}$; $a = 12.01$ (1), $b = 13.46$ (1), $c = 14.52$ (1) Å; $\alpha = 90.6$ (1), $\beta = 111.4$ (1), $\gamma = 102.0$ (1)°; $V = 2128$ Å^3; $\rho_{\text{calcd}} = 1.48$ g cm^{-3}; $Z = 2$; $T = 100$ K. A total of 4968 intensities were measured on a CAD 4 Enraf-Nonius diffractometer in the ω–2θ scan mode with monochromatized Cu Kα radiation ($1 < \theta < 60°$). The crystal structure was refined to a conventional $R(F) = 0.069$ for 1648 reflections having $\sigma(I)/I < 0.33$. The indium atom is bound to the acetato group by two oxygen atoms, leading to an intermediate configuration between five- (4/1) and six-coordination (4/2) (In–O(2) = 2.14 (1) Å, In–O(1) = 2.60 (2) Å, $\langle$In–N$\rangle$ = 2.16 (3) Å), and is displaced 0.61 (2) and 0.68 (2) Å from the four-nitrogen plane and the mean plane of the macrocycle, respectively.

Introduction

Since carbon dioxide is the most abundant source of carbon on the earth, the chemical reactivity of this molecule is of great interest and studies dealing with its chemical fixation have made progress in recent years.[1-4] The reduction of carbon dioxide naturally occurs during photosynthesis in green plants, the overall reaction being the reduction of carbon dioxide to carbohydrate by water. Visible light absorbed by and transferred from tetrapyrrolic pigments (e.g. chlorophylls) provides the energy required for this reduction. Nevertheless, these photosynthetic systems are rather complicated and not yet completely understood. In relation to some aspects of photosynthesis Inoue and Takeda[5] reported the photostimulated interaction of CO_2 with the σ-bonded $(TPP)AlC_2H_5$ complex in the presence of *N*-methylimidazole. By using infrared measurements, they provided in situ characterization of the $(TPP)AlCO_2C_2H_5$ derivative formation.

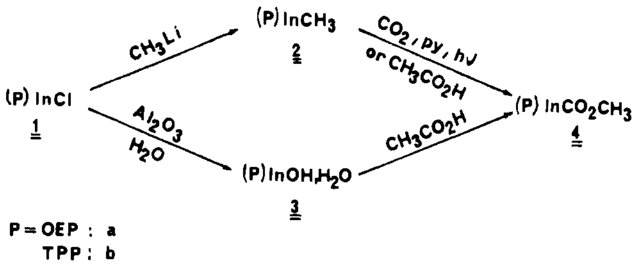
In past years we reported the synthesis, characterization, and reactivity toward sulfur dioxide of a novel series of metal–carbon σ-bonded alkyl(aryl)indium(III) porphyrins, $(P)In^{III}R(Ar)$ (P (porphyrinate(2−)) = OEP (2,3,7,8,12,13,17,18-octaethylporphyrinate(2−)), TPP (5,10,15,20-tetraphenylporphyrinate(2−))).[6-8] In the course of our studies we also observed that carbon dioxide inserts into the indium–carbon σ bond of these complexes under irradiation by visible light in the presence of pyridine, leading to new stable carboxylato compounds. The same products have also been obtained by action of acetic acid on either the σ-bonded alkyl(aryl)indium(III) porphyrins or the aquohydroxoindium(III) porphyrins, $(P)In^{III}OH,H_2O$.

In this paper we report two different syntheses and the characterization of these new (acetato)indium(III) porphyrins. We also describe the molecular stereochemistry of (acetato)(2,3,7,8,12,13,17,18-octaethylporphyrinato)indium(III) established by X-ray diffraction methods. The synthesis of the aquohydroxoindium(III) porphyrins reported in the literature[9,10] was rather complicated, and only partial data were available. Therefore, we propose here a simple preparation and the characterization of these complexes.

Experimental Section

Scheme I summarizes the reactions involved in the synthesis of the new (acetato)indium(III) porphyrins and the numbering used for each complex.

Scheme I



The chloroindium(III) porphyrins (**1**) were synthesized with use of previously published methods,[11,12] and the methylindium(III) porphyrins (**2**) were obtained by the action of methyllithium on compounds **1**.[6] The synthesis of the aquohydroxoindium(III) porphyrins (**3**) was achieved starting from compounds **1** by exchange reaction through a deactivated basic alumina column (eluent toluene) according to the procedure described by Abraham et al.[13] for the preparation of hydroxothallium(III) porphyrins. The $(P)InCO_2CH_3$ derivatives were obtained as follows.

Photochemical Insertion of CO_2 into the In–C σ Bond of $(P)InCH_3$ (2). A gentle stream of carbon dioxide was bubbled through a 0.5 mmol irradiated solution of $(OEP)InCH_3$ (**2a**) (or $(TPP)InCH_3$ (**2b**)) in an anhydrous 60 (110)/30 (55) mL benzene/pyridine mixture for 11 (7) h. To avoid any thermal process, the light source (OSRAM HQI 400 W-71 lamp) was kept 20 cm away from the reactor. The transformation was monitored by TLC (basic alumina, 3/1 chloroform/*n*-hexane). When the reaction was completed, the solvents were removed on a rotavap under reduced pressure and the crude solid was recrystallized in a 2/1 chloroform/ethanol mixture (yield 90%).

Hydrolysis of the In–C σ Bond of $(P)InCH_3$ (2) by CH_3CO_2H.[14] A 25-mL amount of glacial acetic acid was added in a 0.5 mmol refluxed solution of $(OEP)InCH_3$ (**2a**) in 50 mL of anhydrous toluene (or $(TPP)InCH_3$ (**2b**) in 50 mL of anhydrous chloroform) and the mixture was then refluxed for 10 min (or 30 min). The reaction was monitored and

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(1) Vol'pin, M. E.; Kolomnikov, I. S. *Organomet. React.* **1975**, *5*, 313.
(2) Inoue, S.; Yamazaki, N. "Organic and Bio-organic Chemistry of Carbon Dioxide"; Kodansha, Ltd.: Tokyo, 1982.
(3) Ziessel, R. *Nouv. J. Chim.* **1983**, *7*, 613.
(4) Palmer, D. A.; Van Eldik, R. *Chem. Rev.* **1983**, *83*, 651.
(5) Inoue, S.; Takeda, N. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 984.
(6) Cocolios, P.; Guilard, R.; Fournari, P. *J. Organomet. Chem.* **1979**, *179*, 311.
(7) Lecomte, C.; Protas, J.; Cocolios, P.; Guilard, R. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1980**, *B36*, 2769.
(8) Cocolios, P.; Fournari, P.; Guilard, R.; Lecomte, C.; Protas, J.; Boubel, J. C. *J. Chem. Soc., Dalton Trans.* **1980**, 2081.
(9) Treibs, A. *Justus Liebigs Ann. Chem.* **1969**, *728*, 115.
(10) Fuhrhop, J. H.; Kadish, K. M.; Davis, D. G. *J. Am. Chem. Soc.* **1973**, *95*, 5140.
(11) Eaton, S. S.; Eaton, G. R. *J. Am. Chem. Soc.* **1975**, *97*, 3660.
(12) Bhatti, M.; Bhatti, W.; Mast, E. *Inorg. Nucl. Chem. Lett.* **1972**, *8*, 133.
(13) Abraham, R. J.; Barnett, G. H.; Smith, K. M. *J. Chem. Soc., Perkin Trans. 1* **1973**, 2142.
(14) The same reaction occurs with use of any (P)InR(Ar) porphyrin: R = CH_3, CH_2CH_3, $CH(CH_3)_2$, $(CH_2)_3CH_3$, $C(CH_3)_3$; Ar = C_6H_5.

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Table I. Crystal Data

formula	$C_{38}H_{47}N_4O_2In{\cdot}2CHCl_3$
fw	945
cryst syst	triclinic
space group, conditions	$P\bar{1}$, none
cryst dimens, mm	0.15 × 0.10 × 0.08
cryst color	purple
cryst stability	just stable in mother solution, sealed in a glass capillary with a drop of solvent at 100 K
lattice parameters at 100 K	
a, Å (100 K)	12.01 (1)
b, Å	13.46 (1)
c, Å	14.52 (1)
α, deg	90.6 (1)
β, deg	111.4 (1)
γ, deg	102.0 (1)
Z	2
V, Å^3	2128 (6)
d_{calcd}, g/cm^3	1.48
radiation	Cu Kα (λ = 1.54051 Å), graphite monochromator
linear abs coeff, cm^{-1}	64.4
μr_{max}	0.96
temp, K	100
instrument	Enraf-Nonius CAD 4, Enraf low-temperature device
ω range, deg	1–60
octants	$\pm h, \pm k, l$
cryst decay	16% in less than 2 weeks
no. of collected data	4968
no. of data $\sigma(I)/I < 0.33$	1648
no. of parameters	502
data/variable ratio	3.28
LS program	SHELX 76
structure solution	heavy-atom method
$R(F)$	0.069
$R_w(F)$	0.071

the obtained product was isolated as described above.

Reaction of CH_3CO_2H with (P)InOH,H_2O (3). A 0.5-mmol sample of compound **3** was refluxed in 50 mL of glacial acetic acid for several minutes. The acetato complex recrystallized after concentration of the solution by partial evaporation of the solvent on a rotavap under vacuum. The obtained solid was solvated by acetic acid, and elemental analysis was performed on samples dried under vacuum (14 mmHg) at 120 °C for at least 48 h (yield 75%).

Physical Measurements. Elemental analyses were performed by the "Service de Microanalyse du CNRS". Mass spectra were recorded in the electron-impact mode with a Finnigan 3300 spectrometer: ionizing energy 35–70 eV; ionizing current 0.4 mA; source temperature 250–400 °C. ^1H NMR spectra were recorded on a JEOL FX 100 spectrometer. Spectra were measured of complex solutions in 0.5 mL of C_6D_6, C_5D_5N, or $CDCl_3$ with tetramethylsilane as internal reference. Twenty to two hundred scans over 16K points were accumulated for each spectrum at 21 ± 1 °C. Infrared spectra were obtained on a Perkin-Elmer 580 B instrument. Samples were 1% dispersions in CsI pellets or Nujol mulls. Electronic aborption spectra were performed on a Perkin-Elmer 559 spectrophotometer using 5×10^{-3} mol L^{-1} toluene or methylene chloride solutions. The crystal data and details of the crystal structure refinement are given in Table I: two disordered chloroform molecules were found in the asymmetric unit (C(43), C(44), Cl(i) atoms). The low quality of the crystal structure is explained by the bad quality and the instability of crystals. It leads to a very small number of relatively accurate structure factors (NO/NP = 3.28). Further experimental details are given in the supplementary material.

Results

Elemental analysis and mass spectral data (Table II) suggest the formulas (P)InOH,H_2O and (P)$InCO_2CH_3$ for complexes **3** and **4**, respectively. For the former compounds chlorine titration was negative and the fragmentation pattern is indicative of a simultaneous elimination of the hydroxyl group and the water molecule. This result is in accordance with a cis configuration for these moieties, but a choice between a cis coordination and an interaction via a hydrogen bond between OH^- and H_2O is not possible. For compounds **4a** and **4b** the molecular ion is observed and the parent peak corresponds to the $[(P)In]^+$ moiety.

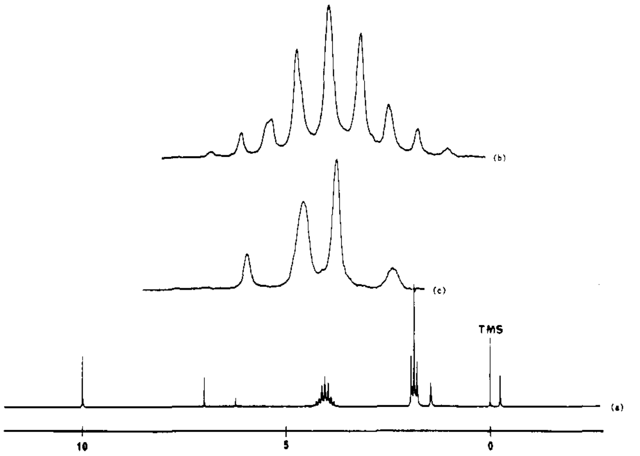

Figure 1. ^1H NMR spectra of (OEP)$InCO_2CH_3$ (**4a**) in $CDCl_3$: (a) spectrum in the −2 to +11 ppm range; (b) experimental trace of A and B methylenic protons; (c) Decoupled trace of A and B methylenic protons.

^1H NMR Measurements. Benzene or pyridine solutions were used for the study of compounds **3a** and **3b**. These complexes show an extremely poor solubility in benzene. This suggests either a strong ionic character for the In–OH bond or the presence of a hydrogen bond between OH^- and H_2O. In the latter case the hydroxyl and water resonance signals may be broadened and rather difficult to observe. Likewise in the aquohydroxothallium(III) porphyrin ^1H NMR spectra,[13] the (P)InOH,H_2O traces do not show any resonance signal for OH^- and H_2O. Nevertheless, such broadness does not occur in the case of the (P)GaOH,H_2O derivatives,[15] which exhibit a sharp peak for OH^- near −4.7 ppm from Me_4Si. In both C_6D_6 and C_5D_5N solvents, complex **3a** spectra show a singlet for the meso, a triplet for the methyl, and multiplet for the methylenic protons (Table III). The latter splitting suggests pentacoordination for this derivative with the metal center above the porphinato core.[16] The complex **3b** gives a singlet for the pyrrole proton resonance, a multiplet for the para and meta phenyl protons, and a broad singlet for the ortho phenyl proton resonance in the region 7.4–9.2 ppm. The ortho proton singlet results from a fast rotation of the phenyl rings indicative of a highly distorted porphinato core.[17] This distortion might be induced by the presence of the bulky HO···HOH group in the axial position.

The acetato complexes obtained by any of the three previously described procedures exhibit the same ^1H NMR spectra. Figure 1 shows the trace of (OEP)$InCO_2CH_3$ (**4a**) (a) in the −2 to +11 region, (b) for the experimental CH_2 multiplet, and (c) for the decoupled CH_2 quadruplet. The methylic protons of the acetato ligand give a singlet at −0.25 ppm (−0.08 ppm for **4b**) from Me_4Si. This shift induced by the porphyrin ring current confirms the axial ligation of the acetato group. Nevertheless, it is much less important compared to that observed for the corresponding indium-methyl complexes (−5.54 ppm for **2a**, −5.14 ppm for **2b**[6]), since in the latter case the absence of the CO_2 molecule between the metal and the methyl group leads to a shorter porphyrin plane–methyl distance. For (OEP)$InCO_2CH_3$ (**4a**) the meso protons display a singlet resonance peak at 10–32 ppm, the methylic protons a triplet at 1.92 ppm, and the methylenic protons a nine-line multiplet centered at 4.17 ppm. This feature results from the nonequivalence of the CH_2 protons and suggests a high magnetic anisotropy between the two sides of the porphyrin plane, normally expected for such pentacoordinated systems. When decoupled (Figure 1c), the CH_2 protons give rise to an AB system with the parameters ν_A = 426.91 Hz, ν_B = 409.39 Hz, $\Delta\nu = \nu_A - \nu_B$ = 17.52 Hz, and J_{AB} = 14.28 Hz. This anisotropy is more

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(15) Coutsolelos, A.; Lecomte, C.; Guilard, R., submitted for publication in *Polyhedron*.

(16) Busby, C. A.; Dolphin, D. *J. Magn. Reson.* **1976**, *23*, 211.

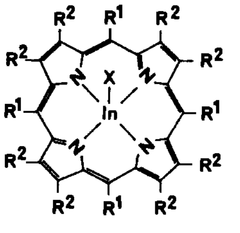
(17) Eaton, S. S.; Fishwild, D. M.; Eaton, G. R. *Inorg. Chem.* **1978**, *17*, 1542.

Table II. Elemental Analyses and Mass Spectral Data

	anal., %[a]				mass spectra		
complex	C	H	N	In	*m/e*	rel intens	frag pattern
(OEP)InOH,H_2O (**3a**)	64.1	6.6	8.0	16.8	682	100.00	$M^{+\cdot}$
	(63.33)	(6.95)	(8.20)	(16.82)	648	12.88	$[M - OH - H_2O + H]^+$
(TPP)InOH,H_2O (**3b**)	69.8	3.9	7.4	14.5	763	100.00	$[M + H]^+$
	(69.30)	(4.11)	(7.34)	(15.06)	727	50.00	$[M - OH - H_2O]^+$
(OEP)$InCO_2CH_3$ (**4a**)	64.3	6.6	7.9	16.1	706	35.50	$M^{+\cdot}$
	(64.58)	(6.72)	(7.92)	(16.25)	647	100.00	$[M - CO_2CH_3]^+$
(TPP)$InCO_2CH_3$ (**4b**)	70.3	3.8	7.0	14.6	786	10.44	$M^{+\cdot}$
	(70.23)	(3.98)	(7.12)	(14.60)	727	100.00	$[M - CO_2CH_3]^+$

[a] Calculated values are given in parentheses.

Table III. ^{1}H NMR Data



X = OH, H_2O or CO_2CH_3

				protons of R^1		protons of R^2		protons of X	
complex	R^1	R^2	X	mult[a]/intens	δ	mult/intens	δ	mult/intens	δ
3a	H	C_2H_5	OH,H_2O	s/4	10.37[b]	t/24	1.82	*e*	
						m/16	3.97		
				s/4	10.68[c]	t/24	1.92	*e*	
						m/16	4.15		
3b	C_6H_5	H	OH,H_2O	s/8	7.93[b] (*o*-H)	s/8	8.90	*e*	
				M/12	7.47 (*m,p*-H)				
				s/8	8.33[c] (*o*-H)	s/8	9.20	*e*	
				M/12	7.79 (*m,p*-H)				
4a	H	C_2H_5	CO_2CH_3	s/4	10.32[d]	t/24	1.92	s/3	−0.25
						m/16	4.17		
4b	C_6H_5	H	CO_2CH_3	m/4	8.09[d] (*o*-H)	s/8	9.02	s/3	−0.08
				m/4	8.36 (*o*′-H)				
				M/12	7.77 (*m,p*-H)				

[a] Legend: s = singlet; t = triplet; q = quadruplet; m = multiplet; M = massive. [b] Solvent C_6D_6. [c] Solvent C_5D_5N. [d] Solvent $CDCl_3$. [e] Signal not observed.

important than that observed for (OEP)InCl (**1a**) ($\Delta\nu$ = 0.74 Hz) and (OEP)$InCH_2CH_3$ ($\Delta\nu$ = 9.16 Hz),[18] but it is of the same magnitude as the one we reported for (OEP)$InSO_3CH_3$ ($\Delta\nu$ = 17 Hz).[8,18] This difference can be attributed to the variation in chemical environment of the indium atom in each examined complex: in the acetato and sulfonato derivatives the two oxygen atoms placed at the same side of the porphyrin plane increase its magnetic anisotropy. Similar information was obtained from the study of (TPP)$InCO_2CH_3$ (**4b**), the ortho phenyl protons displaying two separate resonance signals at 8.09 and 8.36 ppm from Me_4Si.

Infrared Spectroscopy. Hydroxyl group stretching frequencies of hydroxometalloporphyrins appear in the 3580–3640-cm^{-1} range.[19] Broad peaks resulting from hydrogen bonding have been reported between 3580 and 3700 cm^{-1} for the (P)TlOH,H_2O complexes.[13] Otherwise, for (P)GaOH,H_2O, which does not exhibit a hydrogen bond,[15] a sharp peak is observed at 3679 cm^{-1}. As expected, the (P)InOH,H_2O derivatives show a broad vibration at about 3630 cm^{-1} (Table IV). In addition, two weak peaks at 475 and 385 cm^{-1} are attributed to the In–O stretching frequencies.[20]

Identical IR spectra were obtained for the acetato complexes prepared according to the three reported methods. Figure 2 illustrates the IR trace of complex **4a**. As shown in Table IV,

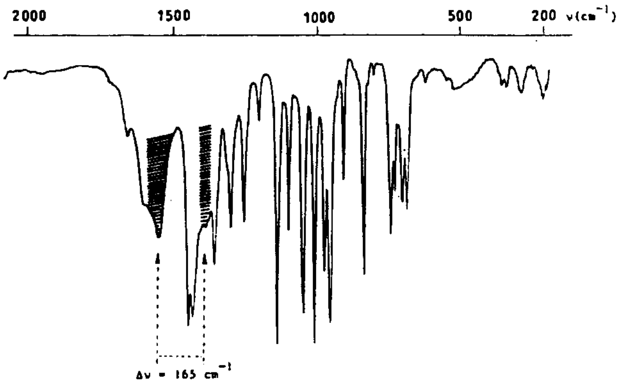
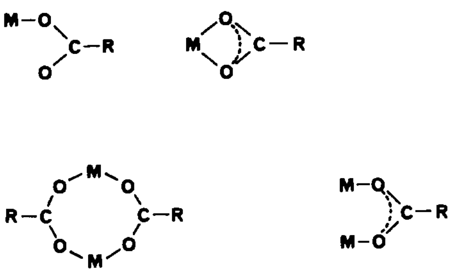


Figure 2. IR spectrum (CsI pellet) of (OEP)$InCO_2CH_3$ (**4a**).

Chart I



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(18) Cocolios, P. Thesis of "Doctorat d'Etat", Dijon, France, 1982.

(19) Buchler, J. W. "Porphyrins and Metalloporphyrins"; Smith, K. M. Ed.; Elsevier: Amsterdam, 1975; p 222.

(20) Habeeb, J. J.; Tuck, D. G. *J. Chem. Soc., Dalton Trans.* **1973**, *243*.

Table IV. Characteristic IR and UV–Visible Spectroscopic Data

	IR		UV–visible[a]				
complex	wavenumber, cm^{-1}	assignt	B(1,0)	B(0,0)	Q(2,0)	Q(1,0)	Q(0,0)
3a	3660	$\nu(OH)$	386[b] (49.1)	408 (396)	500 (2.3)	539 (17.9)	575 (20.5)
	1555	$\delta(HOH)$					
	515	$\rho_w(H_2O)$					
3b	3631	$\nu(OH)$	403[b] (51.4)	426 (502)	520 (4.0)	560 (20.1)	599 (9.5)
	540	$\rho_w(H_2O)$					
	475, 385	$\nu(InO)$					
4a	1570	$\nu_{as}(CO_2^-)$	384[c] (59.5)	406 (441)	496 (4.5)	538 (20.0)	574 (18.5)
	1405	$\nu_s(CO_2^-)$					
	685	$\delta(OCO)$					
	345, 275	$\nu(InO)$					
4b	1562	$\nu_{as}(CO_2^-)$	402[c] (42.9)	424 (615)	519 (4.8)	558 (21.0)	598 (9.5)
	1421	$\nu_s(CO_2^-)$					
	315, 285	$\nu(InO)$					

[a] Values given are of λ (nm) with ε (10^{-3} mol^{-1} L cm^{-1}) in parentheses. [b] Solvent $C_6H_5CH_3$. [c] Solvent CH_2Cl_2.

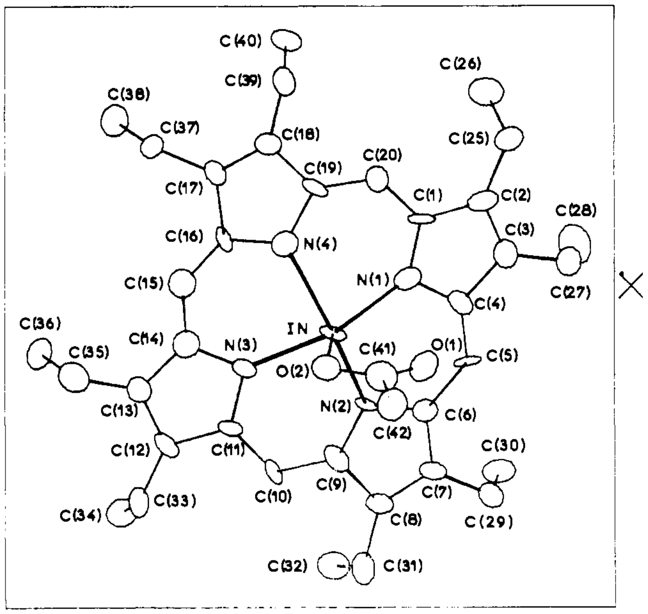
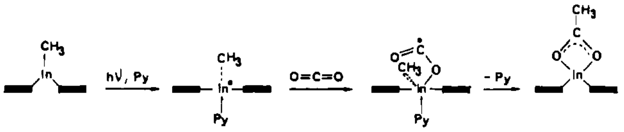


Figure 3. ORTEP[22] view of $(OEP)InCO_2CH_3$.

the $\nu_{as}(CO_2^-)$ and $\nu_s(CO_2^-)$ stretching frequencies are observed at 1570 and 1405 cm^{-1} for complex **4a** and 1562 and 1421 cm^{-1} for complex **4b**. The values of the frequency difference $\Delta\nu$ = 165 cm^{-1} for compound **4a** and $\Delta\nu$ = 141 cm^{-1} for **4b** exclude monoligation.[19,21] Nevertheless, a choice between a bisligated or a dimeric mono- or dibridged complex is not possible. These structural arrangements of metallic carboxylates are depicted in Chart I.

The molecular stereochemistry of compounds **4a** and **4b** was definitely established by X-ray diffraction methods carried out on a monocrystal of $(OEP)InCO_2CH_3$ (**4a**). Final positional parameters of the non-hydrogen atoms are given in Table V, and Figure 3 is an ORTEP[22] view of $(OEP)InCO_2CH_3$. The coordination of the indium atom can be described either by a 4/1 or a 4/2 type. Indeed, this atom is coordinated by the four nitrogen atoms of the macrocycle and by the two oxygen atoms of the acetato group, giving rise to two different interactions: a strong bonding occurs between O(2) and the metal atom (In–O(2) = 2.14 (1) Å) similar to that observed in the covalent complex $(TPP)InCH_3$[7] (In–CH_3 = 2.13 (1) Å) while a weaker interaction appears between the O(1) oxygen atom and the metal (In–O(1) = 2.60 (1) Å). This results in a highly distorted coordination polyhedron with the O(2) oxygen atom, which eclipses the N(3) atom of the porphyrin, displaced from the ideal axial position of 16.3 (6)° (N(3)–In–O(2) = 90.3 (6)° instead of the theoretical value of 106.6°). Furthermore, the O(1) oxygen atom, which eclipses the C(5) atom of the macrocycle, interacts with one of the chloroform molecules by means of a hydrogen bond (O(1)–C(43) = 3.04 (3) Å).

Scheme II



Thermal parameters of the non-hydrogen atoms, calculated hydrogen positional parameters, bond lengths and angles of the compound, least-squares planes, and a list of structure factors are given in the supplementary material.

Discussion

Carbon Dioxide Insertion Mechanism. Both irradiation by visible light and the addition of pyridine are required for the insertion of carbon dioxide into the indium–carbon σ bond of $(P)InCH_3$. Experiments carried out in the dark afforded the starting metalloporphyrin. Attempts to insert CO_2 in the absence of pyridine were also unsuccessful. In order to determine the effect of the added base, UV–visible spectra of benzene or methylene chloride solutions of $(P)InCH_3$ containing increasing amounts of pyridine were recorded. Even in neat pyridine the obtained spectra were identical without any change in wavelength or absorbance maxima, thus implying five-coordinate $(P)InCH_3$ species in all studied media. These results contrast with those obtained for $(TPP)AlCH_2CH_3$, where six-coordinate adducts were obtained upon addition of imidazole.[5] In our case irradiation of argon-saturated benzene/pyridine solutions of $(P)InCH_3$ led to reduction of the complex, as was ascertained by the ESR trace of the photolyzed mixture. The morphology of the ESR spectrum at 130 K similar to those of electroreduced (P)InX (X = Cl, ClO_4)[23] suggests the presence of an indium radical species. ESR spectra have not been observed in neat benzene solutions of $(P)InCH_3$ under the same conditions. In addition electronic absorption spectra characteristic of $(P)InOH,H_2O$ were obtained presumably by fast reaction of the photolyzed indium species with remaining water traces in the solvent. Consequently, we tentatively suggest that the pyridine coordinates to the reduced indium porphyrin, leading to stable $[(P)InCH_3(py)]^\bullet$ six-coordinate species. If that is the case, insertion of CO_2 does not proceed via initial coordination of the molecule to the metal center.[1-4] We may rather assume that the indium radical adds to CO_2 similarly to the addition of its isoelectronic tri-*n*-butylgermyl or tri-*n*-butylstannyl radicals to the C=O bond of carbonyl compounds.[24] The overall

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(21) Nakamoto, K. "Infrared and Raman Spectra of Inorganic and Coordination Compounds", 3rd ed.; Wiley-Interscience: New York, 1978; p 230.

(22) Johnson, C. K. *Oak Ridge Natl. Lab.*, [*Rep.*] *ORNL* (*U.S.*) **1965**, *ORNL-3794*.

(23) Kadish, K. M.; Cornillon, J.-L.; Cocolios, P.; Tabard, A.; Guilard, R. *Inorg. Chem.*, in press.

(24) Ingold, K. U.; Lusztyk, J.; Scaiano, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 343.

Table V. Fractional Coordinates of Non-Hydrogen Atoms (×10⁴), Estimated Standard Deviations (×10⁴), and Equivalent Temperature Factors B_{eq}[a] (Å²)

atom	x	y	z	B_{eq}
In	3301 (2)	1782 (1)	1030 (1)	1.68 (5)
N(1)	4614 (18)	2519 (14)	2427 (14)	2.6 (2)
N(2)	4400 (16)	2771 (12)	365 (12)	1.2 (2)
N(3)	1807 (17)	1920 (13)	9740 (12)	1.9 (2)
N(4)	1959 (18)	1576 (14)	1766 (14)	2.7 (2)
C(1)	4584 (22)	2378 (16)	3341 (16)	1.6 (2)
C(2)	5753 (24)	2767 (19)	4148 (19)	3.0 (2)
C(3)	6498 (22)	3155 (17)	3650 (16)	2.5 (2)
C(4)	5811 (22)	2988 (16)	2592 (16)	2.1 (2)
C(5)	6237 (22)	3251 (16)	1859 (17)	1.9 (2)
C(6)	5635 (21)	3194 (15)	826 (16)	1.7 (2)
C(7)	6119 (22)	3548 (16)	99 (16)	1.9 (2)
C(8)	5210 (22)	3353 (15)	9192 (16)	1.8 (2)
C(9)	4092 (22)	2827 (17)	9385 (16)	2.4 (2)
C(10)	2898 (20)	2479 (16)	8638 (15)	1.7 (2)
C(11)	1812 (21)	2069 (16)	8814 (15)	1.5 (2)
C(12)	626 (22)	1875 (16)	8013 (16)	2.0 (2)
C(13)	9805 (22)	1496 (18)	8484 (17)	2.6 (2)
C(14)	513 (23)	1548 (18)	−476 (19)	2.8 (2)
C(15)	113 (23)	1262 (17)	300 (18)	2.7 (2)
C(16)	736 (20)	1279 (15)	1283 (15)	1.5 (2)
C(17)	229 (22)	1015 (17)	2070 (16)	2.2 (2)
C(18)	1137 (22)	1177 (16)	2945 (17)	2.0 (2)
C(19)	2281 (22)	1578 (16)	2777 (16)	1.9 (2)
C(20)	3477 (21)	1898 (16)	3463 (16)	2.1 (2)
C(25)	5983 (23)	2758 (19)	5203 (18)	2.9 (2)
C(26)	5454 (26)	3508 (22)	5581 (20)	4.4 (2)
C(27)	7828 (22)	3680 (18)	4125 (18)	2.5 (2)
C(28)	8029 (27)	4844 (21)	4332 (21)	4.7 (2)
C(29)	7426 (22)	4115 (16)	311 (16)	2.1 (2)
C(30)	7646 (24)	5212 (17)	655 (18)	2.7 (2)
C(31)	5218 (22)	3557 (18)	8210 (18)	2.8 (2)
C(32)	4782 (24)	4562 (18)	7886 (18)	2.9 (2)
C(33)	374 (21)	1989 (17)	6990 (17)	2.5 (2)
C(34)	279 (24)	3047 (18)	6695 (19)	3.2 (2)
C(35)	8453 (25)	1224 (19)	8015 (18)	3.5 (2)
C(36)	7832 (22)	2137 (18)	8027 (19)	3.1 (2)
C(37)	8856 (21)	655 (17)	1844 (17)	2.3 (2)
C(38)	8222 (23)	1569 (18)	1814 (19)	3.1 (2)
C(39)	1160 (22)	1129 (18)	3931 (18)	2.7 (2)
C(40)	1191 (23)	2120 (18)	4467 (17)	2.9 (2)
O(1)	4996 (16)	746 (13)	1466 (13)	3.5 (2)
O(2)	3048 (15)	213 (11)	553 (11)	2.5 (2)
C(41)	4116 (27)	72 (20)	956 (19)	3.5 (2)
C(42)	4257 (23)	8969 (19)	721 (19)	3.5 (2)
C(43)	6589 (25)	288 (20)	3512 (19)	3.6 (2)
Cl(1)	3076 (7)	845 (6)	6797 (6)	4.6 (2)
Cl(2)	7979 (7)	1064 (5)	4373 (5)	4.4 (2)
Cl(3)	4493 (9)	8 (7)	5927 (7)	6.2 (2)
C(44)	11079 (21)	3868 (18)	2134 (17)	2.5 (2)
Cl(4)	324 (7)	4426 (6)	2775 (5)	4.4 (2)
Cl(5)	609 (8)	4060 (6)	911 (6)	4.9 (2)
Cl(6)	2660 (8)	4280 (6)	2753 (7)	6.5 (2)
Cl(11)	3675	1311	7113	4.1 (2)
Cl(12)	2264	8992	6668	5.0 (2)
Cl(13)	4945	66	−498	4.8 (2)
Cl(14)	−260	4293	1948	4.5 (2)
Cl(15)	1098	4569	1095	4.3 (2)
Cl(16)	2669	4365	3144	5.2 (2)

[a] $B_{eq} = (8/3)\pi^2\sum_{i,j}u_{ij}a_i^*a_j^*\ \vec{a}_i\cdot\vec{a}_j$.

mechanism for insertion of carbon dioxide into the indium–carbon σ bond of (P)InCH$_3$ can be described as shown in Scheme II.

Stereochemistry of the Acetato Group. In the past years, we reported the crystal structures of two other (acetato)metalloporphyrins: (TPP)Nb(O)CO$_2$CH$_3$·CH$_3$COOH[25] and (TpMePP)FeCO$_2$CH$_3$·$^1/_2$CH$_3$COOH.[26] Hoard and co-workers[27] reported also the crystal structures of (OEP)Zr(CO$_2$CH$_3$)$_2$ and (OEP)Hf(CO$_2$CH$_3$)$_2$. Figure 4 shows the different coordinations obtained: the acetato group first can be described as an anionic ligand when it is bonded to nd^0 metals (Sc^{III},[19] Nb^{V},[25] Zr^{IV},[27] Hf^{IV} [27]); in that case the two metal–oxygen bonds are equal (2.22 Å in (TPP)Nb(O)CO$_2$CH$_3$[25] to 2.27 Å in (OEP)Hf(CO$_2$CH$_3$)$_2$[27]) and the metal atom is rigorously in the plane of the acetate group. Furthermore, as pointed out earlier by Buchler,[19] bidentate ligation produces a characteristic IR spectrum with $\Delta\nu(CO_2^-) = \nu_{as}(CO_2^-) - \nu_s(CO_2^-)$ close to or smaller than 150 cm^{-1}. When the acetato ligand is covalently bonded, as for (TpMePP)FeCO$_2$CH$_3$·$^1/_2$CH$_3$COOH, the coordination of the acetate group is end-on and the resulting bond distance (Fe–O = 1.893 (3) Å) is very close to that observed in a dioxygen complex of the iron(II) picket fence porphyrin.[28] The metal atom is out of the acetate plane by 0.066 (8) Å. This end-on coordination implies an IR $\Delta\nu$ of 373 cm^{-1} for (OEP)FeCO$_2$CH$_3$.[26]

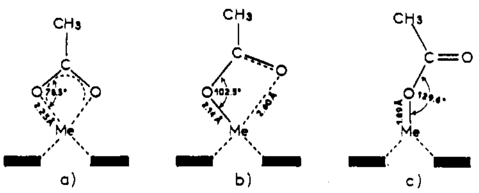

Figure 4. Schematic view of the possible orientations of an acetate group in metalloporphyrin structural chemistry. The oxo ligand of the Nb complex and the second acetate groups of the Zr and Hf derivatives are omitted for clarity.

In (OEP)InCO$_2$CH$_3$, the metal is a spherical 4d^{10} ion and we could expect an ionic bonding as in the nd^0 complexes, which would lead to a bidentate coordination and an IR $\Delta\nu$ close to 150 cm^{-1}. The observed value of 165 cm^{-1} then excluded an end-on coordination. The X-ray structure gives an intermediate coordination due to the interaction with a chloroform molecule. The indium–oxygen distances are In–O(2) = 2.14 (1) Å and In–O(1) = 2.60 (1) Å, and the metal ion lies in the plane of the acetato group. We can postulate that the free (OEP)InCO$_2$CH$_3$ molecule would adopt a bidentate conformation. This assumption is supported by the axial position of the C(41) carbon atom (N(3)–In–C(41) = 114.1 (6)°) and by the nonaxial position of the O(1) oxygen atom: in an end-on coordination the interaction with CHCl$_3$ would have left O(1) in an axial position and displaced the C(41) atom.

Registry No. **2a**, 63288-51-7; **2b**, 63074-31-7; **3a**, 50733-39-6; **3b**, 69377-34-0; **4a**, 96150-60-6; **4b**, 96150-61-7; CO, 124-38-9.

Supplementary Material Available: Detailed description of the crystal structure solution and listings of fractional coordinates of hydrogen atoms, thermal parameters of non-hydrogen atoms, bond distances and angles in the coordination polyhedron, bond distances and angles (complete listing), and observed and calculated structure factors (17 pages). Ordering information is given on any current masthead page.

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(25) Lecomte, C.; Protas, J.; Guilard, R.; Fliniaux, B.; Fournari, P. *J. Chem. Soc., Dalton Trans.* **1979**, 1306.

(26) Oumous, H.; Lecomte, C.; Protas, J.; Cocolios, P.; Guilard, R. *Polyhedron* **1984**, *3*, 651.

(27) Hoard, J. L. "Porphyrins and Metalloporphyrins"; Smith, K. M., Ed.; Elsevier: Amsterdam, 1975; p 347.

(28) Jameson, G. B.; Molinaro, F. S.; Ibers, J. A.; Collman, J. P.; Brauman, J. I.; Rose, E.; Suslik, K. S. *J. Am. Chem. Soc.* **1980**, *102*, 3224.