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Metal–Metal Bonds Extended over a Porphyrin Ring. 1. Syntheses of (TPP)Sn–M(CO)$_{n-1}$–Hg–M(CO)$_n$ and (TPP)In–M(CO)$_n$ (M(CO)$_n$ = Mn(CO)$_5$, Co(CO)$_4$) and X-ray Molecular Structure Analysis of (TPP)Sn–Mn(CO)$_4$–Hg–Mn(CO)$_5$·$^1/_2$CH$_2$Cl$_2$

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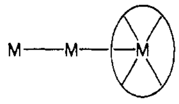
The title compounds have been synthesized by the reaction of (TPP)SnCl$_2$ with Hg[Mn(CO)$_5$]$_2$ and Hg[Co(CO)$_4$]$_2$ or by the reaction of (TPP)InCl with Mn$_2$(CO)$_{10}$ and Co$_2$(CO)$_8$. The structure of (TPP)Sn–Mn(CO)$_4$–Hg–Mn(CO)$_5$ has been solved at room temperature. It crystallizes in the trinclinic system, space group $P\bar{1}$. Its lattice constants are a = 14.79 (4) Å, b = 14.87 (3) Å, c = 13.49 (2) Å, α = 92.3 (2)°, β = 111.3 (2)°, and γ = 109.3 (3)° with Z = 2. The molecule contains a bent four metal atom unit, (TPP)Sn–Mn(1)(CO)$_4$–Hg–Mn(2)(CO)$_5$, extended over the porphyrin ring with a right angle at Mn(1). The observed Sn–Mn bond length, 2.554 (7) Å, is the shortest one yet observed for tin–manganese bonded compounds, and the tin atom lies about 0.85 Å above the plane defined by the four nitrogen atoms of the porphyrin ring. All the synthesized compounds show very strong absorptions at around 450 nm and strong absorptions in the 340–390-nm region. ^{1}H and ^{13}C NMR have been measured for these compounds.

Remarkable development has recently been made in the metal porphyrin derivatives that possess or may possess metal–metal interaction[2] by attracting interest not only from the synthetic aspect[3] but also from the biological significance[4] and from the potential use of the compounds as starting materials to synthesize electron-conducting stacked metal porphyrin polymers.[5] In some of these derivatives, two metal atoms are located at such distance that some sort of metal–metal bond is expectable. For instance, the Re–Re distance in (TPP)[Re(CO)$_3$]$_2$[3a] is 3.13 Å and the Rh–Rh distance in (OEP)[Rh(CO)$_2$]$_2$[3b] is 3.09 Å. However, extended Hückel MO calculations by Tatsumi and Hoffmann[6] showed that the metal–metal overlap population is 0.016 and 0.018, respectively, which is too small to regard the interaction as a metal–metal bond. We therefore were tempted to synthesize new metal porphyrin derivatives in which more than two metal atoms are linked by metal–metal bond (I).[7] The aims of syntheses of these types of compounds are twofold: First, these types of metal porphyrin compounds are considered to be precursors of the metal porphyrin derivatives in which a linear metal framework is sandwiched by two porphyrin ligands (II). Second, these types of compounds are model compounds to study the influence of the porphyrin as a ligand on the metal–metal bond. We have recently reported as a preliminary work the synthesis and the structure of (TPP)Sn–Mn(CO)$_4$–Hg–Mn(CO)$_5$ (**1**) where four metal atoms are linked by metal–metal bonds in a bent fashion,[8] and since then we have synthesized several such new compounds. In the present paper, we report the procedure of the syntheses of these compounds, the detailed structure of **1**, and the spectra of these compounds.



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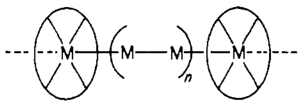

II

Experimental Section

All the syntheses were made under a purified nitrogen atmosphere.[9] All the solvents were distilled under a nitrogen atmosphere from calcium chloride or sodium benzophenone ketyl.

Materials. (Tetraphenylporphyrinato)dichlorotin(IV), (TPP)SnCl$_2$,[10] and (tetraphenylporphyrinato)chloroindium(III), (TPP)InCl,[11] were prepared according to the literature methods. Hg[Mn(CO)$_5$]$_2$[12] and Hg[Co(CO)$_4$]$_2$[13] were also obtained by the literature methods. Cd[Co(CO)$_4$]$_2$ and Zn[Co(CO)$_4$]$_2$ were obtained by the metal-exchange reaction from Hg[Co(CO)$_4$]$_2$.[14] Mn$_2$(CO)$_{10}$, Co$_2$(CO)$_8$, Fe$_2$(CO)$_9$, Fe$_3$(CO)$_{12}$, and Re$_2$(CO)$_{10}$ were purchased from Strem Chemical Co. [Co(CO)$_3$L]$_2$ (L = P(OPh)$_3$) was synthesized by Brown's method.[15]

Syntheses. (TPP)Sn–Mn(CO)$_4$–Hg–Mn(CO)$_5$·$^1/_2$CH$_2$Cl$_2$ (1). An 800-mg sample (1 mmol) of (TPP)SnCl$_2$ was refluxed with 590 mg (1

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Table I. Analytical Data

compd	% C		% H		% N	
	found	calcd	found	calcd	found	calcd
$(TPP)Sn-Mn(CO)_4-Hg-Mn(CO)_5 \cdot {}^1/_2CH_2Cl_2$	47.56	48.08	2.20	2.19	3.83	4.19
$(TPP)Sn-Co(CO)_3-Hg-Co(CO)_4 \cdot CH_2Cl_2$	47.42	46.93	2.39	2.27	4.20	4.21
$(TPP)In-Mn(CO)_5$	64.45	63.95	3.65	3.06	5.69	6.07
$(TPP)In-Co(CO)_4$	63.76	64.16	3.55	3.14	5.73	6.24

mmol) of $Hg[Mn(CO)_5]_2$ in 50 mL of o-$Cl_2C_6H_4$ for 1 h. The color of the solution changed gradually from purple to dark green. The solvent was vacuum stripped to leave a dark purple-green solid. The solid was extracted with 20-mL portions of hot hexane several times, and hexane was distilled off from the combined extracts. The residue was recrystallized from CH_2Cl_2–hexane in a refrigerator to afford 350 mg (yield 27% based on $(TPP)SnCl_2$) of dark purple-green solid. The detailed procedure of the original method to synthesize the same compound from $(TPP)SnCl_2$ and $Mn_2(CO)_{10}$ was described elsewhere.[8]

$(TPP)Sn-Co(CO)_3-Hg-Co(CO)_4 \cdot CH_2Cl_2$ (2). To 800 mg (1 mmol) of $(TPP)SnCl_2$ was added 540 mg (1 mmol) of $Hg[Co(CO)_4]_2$ in 50 mL of THF, and the mixture was refluxed for 12 h. The color of the solution changed from purple to dark green during reflux. The solvent was distilled off at reduced pressure, and the resulting dark green residue was extracted with 20-mL portions of benzene three times. The solvent was vacuum stripped from the combined extracts, and the residue was recrystallized from CH_2Cl_2–petroleum ether in a refrigerator to give 640 mg (yield 51% based on $(TPP)SnCl_2$) of dark purple-green microcrystalline product.

$(TPP)In-Mn(CO)_5$ (3). Method A. A 125-mg sample of $Mn_2(CO)_{10}$ (0.32 mmol) dissolved in 20 mL of THF was stirred over 1% sodium amalgam for 3 h at room temperature. The supernatant greenish gray solution was mixed with 490 mg (0.64 mmol) of (TPP)InCl that was suspended in 30 mL of THF, and the mixture was stirred at room temperature for 3 h. The color of the solution changed immediately to dark green upon mixing. THF was vacuum stripped, and the dark purple green residue was extracted with 20-mL portions of benzene three times. The solvent was completely distilled off at reduced pressure, and the residue was recrystallized from CH_2Cl_2–hexane in a refrigerator to afford 70 mg (yield 12% based on (TPP)InCl) of dark purple-green product.

Method B. A 190-mg sample (0.49 mmol) of $Mn_2(CO)_{10}$ was mixed with an equimolar amount of (TPP)InCl in 30 mL of o-$Cl_2C_6H_4$, and the mixture was refluxed for 3 h. The color of the solution changed from purple to dark green during reflux. The reaction was monitored by taking IR spectra in the carbonyl stretching region. After the solvent was distilled off at reduced pressure, a procedure of purification similar to method A was applied and 200 mg of dark purple green product (yield 44% based on (TPP)InCl) was obtained.

$(TPP)In-Co(CO)_4$ (4). Method A. A 70-mg sample (0.20 mmol) of $Co_2(CO)_8$ dissolved in 30 mL of THF was stirred over 1% sodium amalgam for 2 h. The supernatant brown solution was mixed with 310 mg (0.4 mmol) of (TPP)InCl suspended in 30 mL of THF, and the mixture was stirred at room temperature overnight. THF was vacuum stripped from the resulting dark green solution, and a procedure of purification similar to that of the case of $(TPP)In-Mn(CO)_5$ gave 260 mg (yield 72% based on (TPP)InCl) of dark purple-green microcrystalline product.

Method B. A 160-mg sample (0.47 mmol) of $Co_2(CO)_8$ was refluxed with 360 mg (0.47 mmol) of (TPP)InCl in 50 mL of THF for 2 h. The solution changed from purple to dark green upon refluxing. The reaction was monitored by taking IR spectra in ν(CO) region. After the mixture was cooled to room temperature, THF was removed by vacuum distillation. A procedure of purification similar to that of method B of $(TPP)In-Mn(CO)_5$ afforded 200 mg (yield 47% based on (TPP)InCl) of dark purple-green product.

Reactions. $(TPP)SnCl_2$ with $Cd[Co(CO)_4]_2$. A 620-mg sample (0.78 mmol) of $(TPP)SnCl_2$ was mixed with 350 mg (0.78 mmol) of $Cd[Co(CO)_4]_2$ in 50 mL of THF, and the mixture was refluxed for 3 h. The solution changed from purple to dark green. After a 3-h reflux, no more IR change in the ν(CO) region was detected. The solvent was vacuum distilled off, and a procedure of purification similar to that for **2** gave 420 mg of dark purple-green product. The IR spectrum of this product in the ν(CO) region was essentially identical with that of **2**. However, satisfactory elemental analyses could not be obtained because of the presence of small amount of silicon grease that adhered to the product and was hard to separate from the product by recrystallization and/or column chromatography (the presence of silicon grease was confirmed by ^1H NMR).

$(TPP)SnCl_2$ wtih $Zn[Co(CO)_4]_2$. A 490-mg sample (0.61 mmol) of $(TPP)SnCl_2$ was mixed with 250 mg (0.61 mmol) of $Zn[Co(CO)_4]_2$ in 50 mL of THF, and the mixture was refluxed for 1 h. A procedure of purification similar to that above gave 100 mg of dark purple-green solid (yield 15% based on $(TPP)SnCl_2$). The IR spectrum in the ν(CO) region of this product is essentially identical with that of **2**. However, satisfactory elemental analyses could not be obtained because of the interference with silicon grease.

Table II. IR Data in the CO Stretching Region

compd	ν(CO), cm^{-1}
$(TPP)Sn-Mn(CO)_4-Hg-Mn(CO)_5$[a]	2070 (s), 2030 (w, br), 2004 (s), 1975 (vs), 1925 (s)
$(TPP)Sn-Co(CO)_3-Hg-Co(CO)_4$[b]	2065 (s), 2000 (m), 1975 (vs), 1933 (m)
$(TPP)Sn-Co(CO)_3-Cd-Co(CO)_4$[b]	2065 (s), 2000 (m), 1973 (vs), 1930 (m)
$(TPP)Sn-Co(CO)_3-Zn-Co(CO)_4$[b]	2060 (s), 2000 (m), 1973 (vs), 1935 (m)
$(TPP)In-Mn(CO)_5$[c]	2080 (s), 1995 (m), 1975 (s), 1965 (s)
$(TPP)In-Co(CO)_4$[c]	2075 (s), 2000 (s), 1965 (vs)
$(TPP)In-Re(CO)_5$[c]	2085 (s), 1998 (m), 1985 (s), 1975 (s)
$(TPP)In-Co(CO)_3P(OPh)_3$[c]	1950 (s), 1935 (s)

[a] CH_2Cl_2 solution. [b] THF solution. [c] Nujol mull.

(TPP)InCl with $[Co(CO)_3P(OPh)_3]_2$. A 340-mg sample (0.38 mmol) of $[Co(CO)_3P(OPh)_3]_2$ was mixed with 280 mg (0.44 mmol) of (TPP)InCl, and the mixture was refluxed in 50 mL of THF for 1 h. A similar procedure of purification afforded 100 mg (yield 19% based on (TPP)InCl) of dark purple-green product. However, satisfactory carbon analysis was not obtained for $(TPP)In-Co(CO)_3P(OPh)_3$ (**5**).

(TPP)InCl with $Re_2(CO)_{10}$. A 340-mg sample (0.52 mmol) of $Re_2(CO)_{10}$ was heated with 400 mg (0.52 mmol) of (TPP)InCl in 30 mL of o-$Cl_2C_6H_4$ at reflux temperature for 2 h. A similar procedure of purification gave 60 mg of dark purple-green solid (yield 11% based on (TPP)InCl for $(TPP)In-Re(CO)_5$).

(TPP)InCl with $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$. A 125-mg sample (0.34 mmol) of $Fe_2(CO)_9$ or 170 mg (0.34 mmol) of $Fe_3(CO)_{12}$ and 260 mg (0.34 mmol) of (TPP)InCl were suspended in 40 mL of THF, and the mixture was heated at reflux temperature for 5 min. The color of the solution changed immediately to dark green, and the IR spectrum in the ν(CO) region was completely identical with that of authentic $Fe(CO)_5$. After evaporation of the solvent at reduced pressure, attempts were made to isolate any product that contained an iron carbonyl moiety except $Fe(CO)_5$, but the efforts were fruitless. Presumably $Fe(CO)_5$ was the only iron carbonyl derivative, and this was distilled off when the solvent was vacuum-stripped, or the iron carbonyl porphyrin derivative, which should be produced, might be too unstable to isolate in our hands.

Spectral Measurements. IR spectra were recorded on a Jasco 701G infrared spectrometer with 0.1-mm NaCl windowed liquid cells. Absorption spectra were obtained with a Shimadzu MPS-5000 spectrometer and a Hitachi 220A spectrometer with 1-mm quartz cells and CH_2Cl_2 as a solvent. ^1H and ^{13}C NMR data were collected with a Hitachi Perkin-Elmer R-20B, a JEOL R90X, and/or a Variant XL200 spectrometer. $CDCl_3$ and toluene-d were employed as solvents with Me_4Si standard. The results of elemental analyses are tabulated in Table I, and the IR and absorption data are collated in Tables II and III, respectively. NMR results are listed in Table IV.

X-ray Molecular Structure Analysis of 1. Dark purple crystals were grown up from dichloromethane–petroleum ether. A crystal of approximate dimensions $0.24 \times 0.40 \times 0.24$ mm^3 was mounted on a Rigaku AFC-5 automated four-circle diffractometer equipped with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The crystal was triclinic with cell constants a = 14.79 (4) Å, b = 14.87 (3) Å, c = 13.49 (2) Å, α = 92.3 (2)°, β = 111.3 (2)°, γ = 109.3 (3)°, V = 2564 (11) Å^3, and Z = 2. Presumably broad diffraction peak profiles are responsible for the large standard deviations with the cell constants. A total of 5419 independent reflections with $|F_o| > 3\sigma(|F_o|)$ were obtained at room temperature by using the θ–2θ scan technique up to 2θ = 55°.

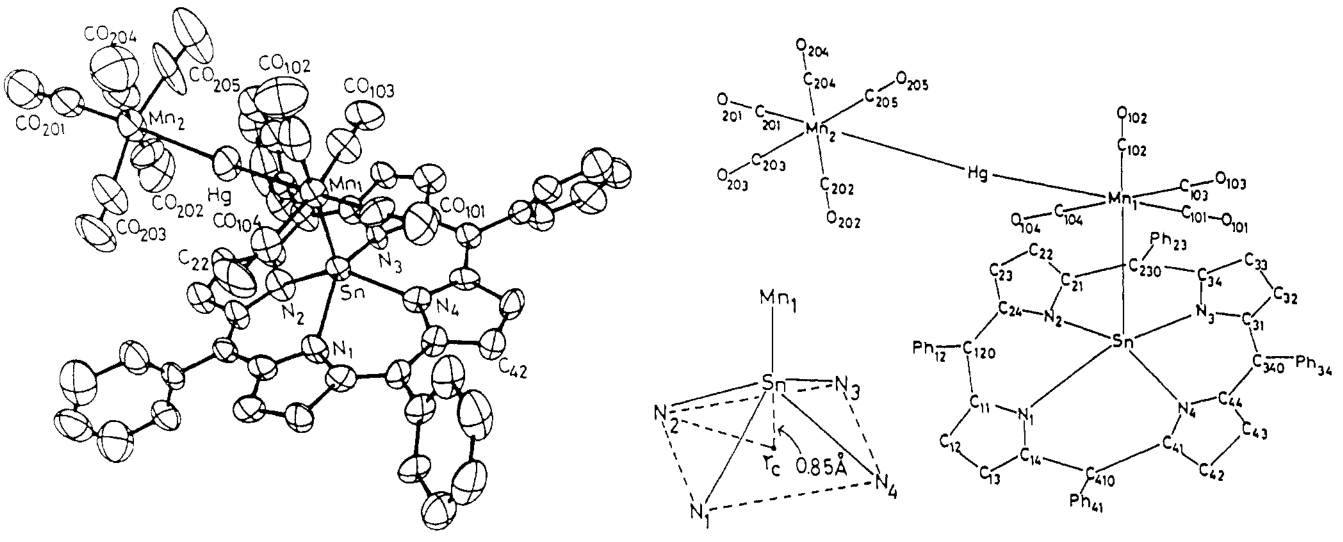

Figure 2. Molecular structure and atom-numbering scheme of **1**. Thermal ellipsoids are drawn at the 50% probability level.

Table III. Absorption Spectral Data in CH_2Cl_2

compd	λ_{max}, nm (ϵ, M^{-1} cm^{-1})
(TPP)Sn-Mn$(CO)_4$-Hg-Mn$(CO)_5$	370 (13 000), 410 (sh), 420 (Soret), 425 (sh), 460 (42 000), 530 (1900), 560 (1600), 600 (2400), 660 (2600)
(TPP)Sn-Co$(CO)_3$-Hg-Co$(CO)_4$	340 (32 000), 410 (sh), 428 (Soret), 450 (sh), 565 (11 000), 605 (8300), 660 (3300)
(TPP)Sn-Co$(CO)_3$-Cd-$(CO)_4$	350 (39 000), 410 (sh), 428 (Soret), 460 (sh), 565 (10 000), 605 (9000), 660 (5000)
(TPP)$SnCl_2$	410 (sh), 432 (Soret), 530 (1200), 565 (5500), 610 (4000)
(TPP)In-Mn$(CO)_5$	395 (52 000), 428 (Soret), 463 (95 000), 565 (5800), 600 (5800), 640 (8000)
(TPP)In-Co$(CO)_4$	375 (17 000), 410 (sh), 430 (Soret), 450 (140 000), 570 (12 000), 630 (7000)
(TPP)In-Re$(CO)_5$	385 (80 000), 425 (Soret), 457 (150 000), 555 (9800), 593 (11 000), 625 (12 600)
(TPP)In-Co$(CO)_3$-P$(OPh)_3$	383 (51 000), 400 (sh), 425 (Soret), 450 (150 000), 560 (13 000), 580 (11 000), 625 (11 000)
Hg$[Mn(CO)_5]_2$	345 (8500)
Hg$[Co(CO)_4]_2$	325 (29 000)

Absorption corrections were applied. The structure was solved by the standard heavy-atom method and refined based on the $P\bar{1}$ space group by the use of the UNICS-III program package and a HITAC M-180 computer. A series of block-diagonal least-squares refinements for 73 non-hydrogen atoms with anisotropic temperature factors reduced R to 0.094 and R_w to 0.113, where anomalous dispersion corrections for Hg, Sn, and Mn were applied. The final positional parameters and values are listed in Table V. The anisotropic thermal parameters and values of F_o vs. F_c are available as supplementary material. The crystal packing in a unit cell is shown in Figure 1 (supplementary material), and the molecular structure of **1** together with the atom-numbering scheme is exhibited in Figure 2. The unit cell contains two molecules of **1** and one CH_2Cl_2 molecule, which is disordered and located at two sites related by the center of symmetry with occupancy factor 0.5.

Results and Discussion

Syntheses. As described in the Experimental Section, the reaction of (TPP)$SnCl_2$ with Hg$[Mn(CO)_5]_2$ and/or M$[Co(CO)_4]_2$ gives (TPP)Sn–Mn$(CO)_4$–Hg–Mn$(CO)_5$ and/or (TPP)Sn–Co$(CO)_3$–M–Co$(CO)_4$ (M = Zn, Cd, Hg) type compounds. The reaction of (TPP)InCl with NaMn$(CO)_5$ or $Mn_2(CO)_{10}$ yields (TPP)In–Mn$(CO)_5$, and the reaction of (TPP)InCl with NaCo$(CO)_4$ or $Co_2(CO)_8$ yields (TPP)In–Co$(CO)_4$. Similarly, the treatment of (TPP)InCl with $[Co(CO)_3P(OPh)_3]_2$ affords (TPP)In–Co$(CO)_3$P$(OPh)_3$, and the treatment of (TPP)InCl with $Re_2(CO)_{10}$ affords (TPP)In–Re$(CO)_5$; these products are believed to be obtained on the basis of spectral results, although satisfactory elementary analyses have not yet been obtained. All these compounds are diamagnetic judging from their NMR spectra. These syntheses show that tetraphenylporphyrin is a good ligand to construct the metal–metal bond.

Description of the Structure of 1. Figure 2 shows a view of the unique structure of (TPP)Sn–Mn$(CO)_4$–Hg–Mn$(CO)_5$ that has

Table IV. NMR Data (δ)

(a) ^1H NMR

compd	β-pyrrole	ortho	meta, para	compd	β-pyrrole	ortho	meta, para
(TPP)Sn-Mn$(CO)_4$-Hg-Mn$(CO)_5$[a]	9.37 9.32	8.5	7.83	(TPP)In-Mn$(CO)_5$[b]	9.01	8.22 8.19	7.77
(TPP)Sn-Co$(CO)_3$-Hg-Co$(CO)_4$[a]	9.28	8.35	7.75	(TPP)In-Co$(CO)_4$[b]	9.08	8.31 8.22	7.81

(b) ^{13}C NMR[c]

compd	α	β	meso	C(1)	C(2)	C(3)	C(4)
(TPP)Sn-Mn$(CO)_4$-Hg-Mn$(CO)_5$	148.5	132.7 132.4	122.0	140.9	135.1 133.7	127.0	128.4
(TPP)Sn-Co$(CO)_4$-Hg-Co$(CO)_4$	148.8	132.7	121.9	140.9	135.1 133.8	127.0	128.4
(TPP)$SnCl_2$	146.0	133.0	121.0	141.0	135.0	127.0	128.5
(TPP)In-Mn$(CO)_5$	149.8	132.2	121.7	142.4	135.0 134.1	126.6	127.7
(TPP)In-Co$(CO)_4$	149.7	132.5	122.1	142.1	135.1 134.0	126.7	127.8
(TPP)InCl	149.5	132.8	121.8	141.8	135.1 134.3	126.9 126.7	128.0

[a] Toluene-*d* solution. [b] Chloroform-*d* solution. [c] Chemical shifts from Me_4Si.

Table V. Atomic Parameters[a]

atom	*x*	*y*	*z*	B_{eq}
Hg	3654 (1)	1243 (1)	5339 (1)	5.0
Sn	1744 (1)	345 (1)	2425 (1)	3.1
Mn(1)	2468 (2)	−403 (2)	4061 (2)	3.5
Mn(2)	4788 (2)	2658 (2)	7059 (3)	4.9
N(1)	204 (10)	346 (9)	2164 (11)	3.7
C(11)	26 (12)	995 (12)	2793 (13)	3.7
C(12)	−927 (13)	556 (12)	2907 (14)	4.1
C(13)	−1385 (13)	−392 (12)	2332 (14)	4.2
C(14)	−684 (12)	−531 (11)	1869 (14)	3.8
N(2)	2121 (10)	1916 (9)	2694 (12)	4.4
C(21)	3099 (12)	2590 (10)	2886 (14)	3.8
C(22)	3214 (14)	3486 (11)	3446 (16)	4.7
C(23)	2371 (14)	3373 (12)	3645 (16)	4.9
C(24)	1648 (12)	2380 (12)	3154 (14)	4.0
N(3)	2807 (9)	756 (8)	1588 (11)	3.4
C(31)	2989 (12)	87 (12)	1007 (13)	3.7
C(32)	4025 (14)	470 (14)	1059 (15)	4.9
C(33)	4484 (13)	1390 (12)	1675 (15)	4.3
C(34)	3724 (13)	1562 (11)	2027 (14)	4.0
N(4)	840 (9)	−764 (9)	983 (10)	3.6
C(41)	−220 (12)	−1431 (11)	691 (12)	3.3
C(42)	−471 (13)	−2190 (12)	−153 (13)	4.1
C(43)	390 (14)	−2056 (12)	−378 (14)	4.7
C(44)	1194 (12)	−1189 (12)	341 (13)	3.7
C(120)	703 (12)	1955 (11)	3248 (13)	3.4
C(230)	3881 (12)	2398 (11)	2623 (15)	4.0
C(340)	2236 (12)	−851 (11)	422 (13)	3.6
C(410)	−870 (12)	−1347 (11)	1167 (13)	3.6
C(121)	374 (13)	2551 (13)	3867 (14)	4.4
C(122)	507 (16)	2395 (15)	4890 (16)	5.7
C(123)	188 (20)	2974 (19)	5528 (22)	8.7
C(124)	−295 (18)	3562 (17)	5023 (21)	8.0
C(125)	−468 (24)	3663 (20)	3962 (26)	10.2
C(126)	−112 (18)	3156 (15)	3354 (17)	6.0
C(231)	4936 (13)	3175 (11)	3031 (15)	4.3
C(232)	5725 (15)	3002 (15)	3832 (18)	6.3
C(233)	6811 (17)	3735 (19)	4292 (24)	9.6
C(234)	6977 (16)	4561 (17)	3813 (21)	8.3
C(235)	6143 (22)	4708 (15)	2972 (24)	9.7
C(236)	5063 (16)	3998 (12)	2505 (20)	6.1
C(341)	2525 (13)	−1479 (13)	−195 (12)	3.6
C(342)	2435 (13)	−2382 (12)	64 (15)	4.6
C(343)	2719 (16)	−2983 (15)	−472 (19)	6.5
C(344)	2987 (16)	−2696 (17)	−1365 (20)	7.1
C(345)	3023 (17)	−1818 (19)	−1649 (19)	7.4
C(346)	2824 (15)	−1159 (15)	−1036 (17)	5.3
C(411)	−1814 (12)	−2196 (12)	978 (14)	4.0
C(412)	−2773 (13)	−2117 (14)	502 (15)	5.2
C(413)	−3736 (16)	−2933 (15)	277 (17)	6.2
C(414)	−3584 (15)	−3795 (16)	580 (17)	6.8
C(415)	−2602 (17)	−3875 (14)	1070 (20)	6.8
C(416)	−1671 (14)	−3060 (13)	1282 (16)	5.1
C(101)	1673 (13)	−1549 (13)	3219 (15)	4.8
O(101)	1159 (11)	−2319 (9)	2697 (12)	6.6
C(102)	2903 (17)	−931 (16)	5168 (18)	6.5
O(102)	3200 (13)	−1323 (13)	5941 (13)	8.5
C(103)	3601 (14)	−198 (12)	3772 (15)	4.5
O(103)	4334 (10)	−119 (11)	3579 (11)	6.3
C(104)	1484 (15)	−238 (13)	4471 (15)	4.7
O(104)	849 (12)	−114 (12)	4722 (13)	7.4
C(201)	5470 (15)	3567 (15)	8229 (16)	5.9
O(201)	5912 (12)	4198 (12)	8980 (14)	8.7
C(202)	4923 (17)	3506 (15)	6212 (16)	6.2
O(202)	5088 (15)	4103 (12)	5689 (14)	9.3
C(203)	3470 (16)	2640 (15)	6817 (19)	6.2
C(203)	2686 (12)	2619 (13)	6705 (15)	8.8
C(204)	4610 (17)	1711 (14)	7807 (17)	5.8
O(204)	4502 (16)	1092 (13)	8275 (14)	9.7
C(205)	5884 (18)	2463 (15)	6943 (23)	8.5
O(205)	6597 (14)	2362 (13)	6861 (19)	11.6
Cl(1)	−136 (13)	5085 (11)	1665 (17)	11.6
Cl(2)	1715 (13)	5052 (11)	1512 (18)	11.9
C(1)	1062 (62)	5520 (34)	1763 (72)	15.9

[a] Positional parameters are multiplied by 10^4. Thermal parameters are given by the equivalent temperature factors (Å^2).

Table VI. Selected Bond Distances (Å) for (TPP)Sn–Mn(CO)$_4$–Hg–Mn(CO)$_5$

Sn–Mn(1)	2.554 (3)	C(13)–C(14)	1.454 (26)
Mn(1)–Hg	2.582 (3)	N(2)–C(21)	1.382 (25)
Hg–Mn(2)	2.659 (3)	N(2)–C(24)	1.397 (25)
Sn–N(1)	2.175 (15)	C(21)–C(22)	1.432 (29)
Sn–N(2)	2.195 (16)	C(22)–C(23)	1.328 (31)
Sn–N(3)	2.196 (14)	C(23)–C(24)	1.458 (29)
Sn–N(4)	2.165 (14)	N(3)–C(31)	1.395 (23)
Mn(1)–C(101)	1.768 (20)	N(3)–C(34)	1.382 (24)
Mn(1)–C(102)	1.730 (25)	C(31)–C(32)	1.419 (28)
Mn(1)–C(103)	1.790 (20)	C(32)–C(33)	1.382 (29)
Mn(1)–C(104)	1.814 (22)	C(33)–C(34)	1.455 (28)
Mn(2)–C(201)	1.762 (22)	N(4)–C(41)	1.444 (22)
Mn(2)–C(202)	1.746 (25)	N(4)–C(44)	1.389 (23)
Mn(2)–C(203)	1.845 (25)	C(41)–C(42)	1.422 (25)
Mn(2)–C(204)	1.770 (25)	C(42)–C(43)	1.367 (28)
Mn(2)–C(205)	1.797 (32)	C(43)–C(44)	1.437 (28)
C(101)–O(101)	1.164 (26)	C(11)–C(120)	1.398 (25)
C(102)–O(102)	1.226 (31)	C(21)–C(230)	1.433 (27)
C(103)–O(103)	1.173 (26)	C(31)–C(340)	1.433 (25)
C(104)–O(104)	1.171 (28)	C(41)–C(410)	1.370 (25)
C(201)–O(201)	1.171 (29)	C(14)–C(410)	1.393 (26)
C(202)–O(202)	1.173 (33)	C(24)–C(120)	1.385 (26)
C(203)–O(203)	1.102 (32)	C(34)–C(230)	1.357 (28)
C(204)–O(204)	1.138 (34)	C(44)–C(340)	1.413 (25)
C(205)–O(205)	1.155 (41)	C(120)–C(121)	1.498 (26)
N(1)–C(11)	1.409 (23)	C(230)–C(231)	1.483 (28)
N(1)–C(14)	1.425 (24)	C(340)–C(341)	1.488 (26)
C(11)–C(12)	1.412 (26)	C(410)–C(411)	1.468 (26)
C(12)–C(13)	1.396 (27)		

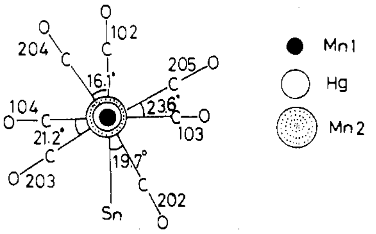

Figure 3. Conformational arrangement of the carbonyl groups on two manganese atoms for **1**.

a four metal atom unit, Sn–Mn(1)–Hg–Mn(2), over the TPP ring. The typical bond lengths and angles are listed in Tables VI and VII, respectively. The phenyl C–C distances and angles are available as supplementary material. The Mn(1)–Hg–Mn(2) array is only slightly bent upward (164.4 (1)°) from the porphyrin ring, while the Sn–Mn(1)–Hg skeleton is bent at virtually a right angle (94.5 (1)°). The plane containing the Sn–Mn(1)–Hg–Mn(2) array passes through two pyrrole rings close to C(22), N(2), N(4), and C(42) atoms. The Hg atom is too far from C(22) and N(2) atoms to expect strong interaction. The tin atom is five-coordinated in a square-pyramidal array. The two Mn atoms are octahedrally coordinated with CO and metal atoms. The conformational arrangement of the equatorial carbonyl groups about the two Mn atoms is intermediate between eclipsed and staggered (Figure 3). The deviation from the eclipsed conformation is estimated by the intersecting angle of the two planes that contain Hg–Mn(2)–C(*i*) (*i* = 202–205) and Hg–Mn(1)–C(*j*) (*j* = 102–104) and/or Hg–Mn(1)–Sn. The angles average 20.3 (27)°.

The observed Sn–Mn(1), Mn(1)–Hg, and Hg–Mn(2) distances are typical for relevant metal–metal bonds.[16,17] The observed Sn–Mn(1) bond length, 2.554 (3) Å, is the shortest one yet observed for a tin–manganese bond;[16] the shortest Sn–Mn bond length is 2.590 Å in Cl$_3$Sn–Mn(CO)$_5$[16] to our knowledge. The adjacent Mn(1)–Hg bond length to the Sn–Mn(1) bond is significantly shorter (about 0.03 Å) than that of the parent compound, Hg[Mn(CO)$_5$]$_2$,[17] while the terminal Hg–Mn(2) bond

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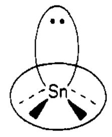
Table VII. Selected Bond Angles (deg) for (TPP)Sn-Mn(CO)$_4$-Hg-Mn(CO)$_5$

Sn-Mn(1)-Hg	94.5 (1)	N(1)-C(11)-C(120)	124.6 (16)
Mn(1)-Hg-Mn(2)	164.4 (1)	N(1)-C(14)-C(410)	124.2 (16)
Mn(1)-Sn-N(1)	112.3 (4)	N(2)-C(21)-C(230)	125.2 (17)
Mn(1)-Sn-N(2)	117.6 (4)	N(2)-C(24)-C(120)	126.6 (17)
Mn(1)-Sn-N(3)	111.5 (4)	N(3)-C(31)-C(340)	125.1 (16)
Mn(1)-Sn-N(4)	110.2 (4)	N(3)-C(34)-C(230)	126.5 (18)
N(1)-Sn-N(2)	80.7 (6)	N(4)-C(41)-C(410)	125.0 (16)
N(2)-Sn-N(3)	81.9 (6)	N(4)-C(44)-C(340)	124.6 (16)
N(3)-Sn-N(4)	80.9 (5)	N(1)-C(11)-C(12)	111.6 (16)
N(1)-Sn-N(4)	81.7 (5)	C(11)-C(12)-C(13)	107.1 (16)
N(1)-Sn-N(3)	136.1 (5)	C(12)-C(13)-C(14)	107.5 (16)
N(2)-Sn-N(4)	132.2 (6)	N(1)-C(140)-C(13)	108.8 (15)
Hg-Mn(1)-C(101)	178.2 (7)	C(12)-C(11)-C(120)	123.8 (17)
Hg-Mn(1)-C(102)	86.8 (8)	C(13)-C(14)-C(410)	126.7 (17)
Hg-Mn(1)-C(103)	81.4 (7)	N(2)-C(21)-C(22)	108.5 (17)
Hg-Mn(1)-C(104)	83.5 (7)	C(21)-C(22)-C(23)	109.8 (19)
Sn-Mn(1)-C(101)	87.3 (7)	C(22)-C(23)-C(24)	106.5 (19)
Sn-Mn(1)-C(102)	177.5 (8)	N(2)-C(24)-C(23)	108.7 (17)
Sn-Mn(1)-C(103)	88.3 (7)	C(22)-C(21)-C(230)	126.3 (18)
Sn-Mn(1)-C(104)	86.6 (7)	C(23)-C(24)-C(120)	124.4 (18)
C(101)-Mn(1)-C(102)	91.7 (11)	N(3)-C(31)-C(32)	110.6 (16)
C(101)-Mn(1)-C(103)	98.5 (9)	C(31)-C(32)-C(33)	106.3 (18)
C(101)-Mn(1)-C(104)	96.8 (10)	C(32)-C(33)-C(34)	108.0 (17)
C(102)-Mn(1)-C(103)	94.1 (10)	N(3)-C(34)-C(33)	108.2 (16)
C(102)-Mn(1)-C(104)	91.3 (11)	C(32)-C(31)-C(340)	124.3 (17)
C(103)-Mn(1)-C(104)	163.6 (10)	C(33)-C(34)-C(230)	125.2 (18)
Hg-Mn(2)-C(201)	176.1 (7)	N(4)-C(41)-C(42)	109.3 (15)
Hg-Mn(2)-C(202)	90.1 (8)	C(41)-C(42)-C(43)	109.0 (17)
Hg-Mn(2)-C(203)	80.2 (8)	C(42)-C(43)-C(44)	106.0 (17)
Hg-Mn(2)-C(204)	84.6 (8)	N(4)-C(44)-C(43)	112.1 (16)
Hg-Mn(2)-C(205)	84.5 (10)	C(42)-C(41)-C(410)	125.7 (16)
C(201)-Mn(2)-C(202)	92.3 (11)	C(43)-C(44)-C(340)	123.3 (17)
C(201)-Mn(2)-C(203)	96.7 (11)	C(11)-C(120)-C(24)	123.8 (17)
C(201)-Mn(2)-C(204)	93.2 (11)	C(11)-C(120)-C(121)	117.4 (16)
C(201)-Mn(2)-C(205)	98.7 (13)	C(24)-C(120)-C(121)	118.8 (16)
C(202)-Mn(2)-C(203)	90.2 (11)	C(21)-C(230)-C(34)	124.7 (18)
C(202)-Mn(2)-C(204)	174.4 (12)	C(21)-C(230)-C(231)	117.3 (17)
C(202)-Mn(2)-C(205)	87.1 (13)	C(34)-C(230)-C(231)	117.9 (18)
C(203)-Mn(2)-C(204)	90.4 (11)	C(31)-C(340)-C(44)	122.8 (16)
C(203)-Mn(2)-C(205)	164.5 (13)	C(31)-C(340)-C(341)	119.4 (16)
C(204)-Mn(2)-C(205)	90.9 (13)	C(44)-C(340)-C(341)	117.6 (16)
Sn-N(1)-C(11)	124.0 (12)	C(14)-C(410)-C(41)	125.2 (17)
Sn-N(1)-C(14)	121.7 (11)	C(14)-C(410)-C(411)	116.6 (16)
Sn-N(2)-C(21)	123.1 (13)	Mn(1)-C(101)-O(101)	177.6 (18)
Sn-N(2)-C(24)	125.0 (13)	Mn(1)-C(102)-O(102)	178.8 (22)
Sn-N(3)-C(31)	123.6 (11)	Mn(1)-C(103)-O(103)	176.2 (18)
Sn-N(3)-C(34)	120.9 (12)	Mn(1)-C(104)-O(104)	178.5 (20)
Sn-N(4)-C(41)	125.2 (11)	Mn(2)-C(201)-O(201)	177.2 (20)
Sn-N(4)-C(44)	128.7 (11)	Mn(2)-C(202)-O(202)	175.3 (23)
C(11)-N(1)-C(14)	105.8 (14)	Mn(2)-C(203)-O(203)	177.6 (23)
C(21)-N(2)-C(24)	106.5 (16)	Mn(2)-C(204)-O(204)	178.6 (24)
C(31)-N(3)-C(34)	106.9 (14)	Mn(2)-C(205)-O(205)	178.2 (29)
C(41)-N(4)-C(44)	103.6 (13)		

length is significantly longer (about 0.05 Å) than that of the parent compound.[17]

The essentially equivalent Sn-N(pyrrole) distance (2.18 (1) Å as an average) is shorter than those in stannic bis(phthalocyanine) (2.347 (7) Å)[18] and longer than those in (TPP)Sn[Re(CO)$_3$(C)$_2$]$_2$ (2.07 (2) Å),[19] (TPP)SnCl$_2$ (2.098 (2) Å),[20] and/or (OEP)SnCl$_2$ (2.082 (2) Å).[21] The average N-Sn-N bond angle is 81.3 (9)°. The tin atom lies 0.85 Å above the plane defined by the four nitrogen atoms. The geometry around the tin atom in **1** is close to that of (Pc)Sn;[22] the tin atom lies 1.11 Å above the plane defined by the four isoindole nitrogen atoms, and the average tin-nitrogen bond length is 2.25 (1) Å and a lone pair of electrons on the tin atom is supposed to be accommodated in the orbital extended above the phthalocyanine ring (III) in



III

(Pc)Sn.[22] The similarity of the geometry and the 18-electron account rule about the Mn(1) atom suggest that the tin atom in **1** has a lone pair of electrons and this pair of electrons is donated from the tin atom to the Mn(1) atom; that is, the tin-manganese bond is composed of a donor-acceptor type bond, with the (TPP)Sn group regarded as a sort of ligand to the Mn(1) atom. A few examples indicate that the donor-acceptor type metal-metal interaction causes the resulting metal-metal bond to be shorter than the ordinary single metal-metal bond.[23] This shortening

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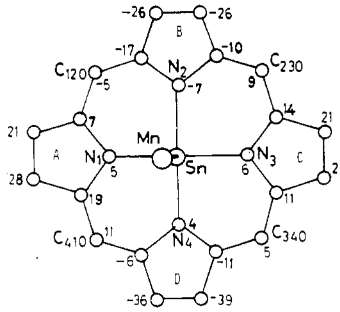

Figure 4. Perpendicular displacement of each atom (in units of 0.01 Å) from the mean plane of 24-atom core. The core in the diagram has the same orientation as that in Figure 2 (right). Positive values for the displacement indicate a displacement on the metal–metal bond side of the plane.

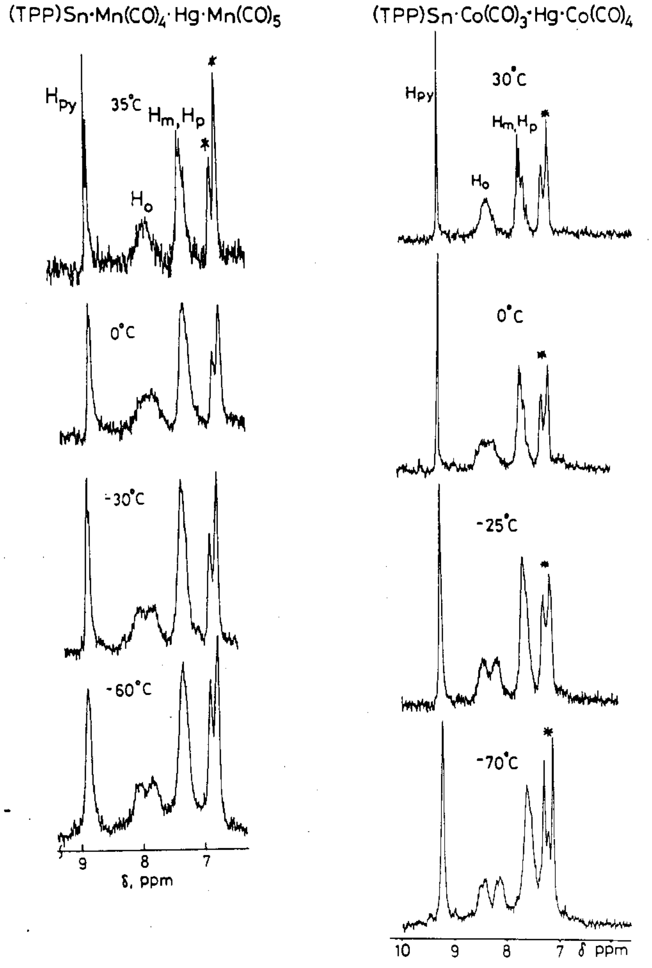

Figure 5. Temperature-dependent ^1H NMR spectra for **1** and **2**. Asterisks show solvent peaks.

is explained in terms of the π back-donation of electrons from the acceptor metal atom to the donor metal atom to mitigate the accumulation of electrons on the acceptor metal atom. The finding that the Sn–Mn(1) and Mn(1)–Hg bonds are shorter than ordinary Sn–Mn and Hg–Mn bonds is explained in terms of the π back-donation from the Mn(1) atom to Sn and Hg atoms. There is no reason to doubt that similar donor–acceptor type bonds are formed between Sn and Co and between Co and Hg atoms in **2**.[24] The observed Mn–C and C–O bond lengths compare well with similar manganese carbonyl derivatives.[16,17] The carbonyl groups tend to decline to the relevant Mn–M bond (M = Hg, Sn). All the bond lengths and bond angles associated with TPP fall in the range reported for similar metalloporphyrin derivatives.[2,19-21] Figure 4 shows the perpendicular displacements of the atoms of the porphyrinato core from the least-squares plane of the 24-atom core. The pyrrole rings A and C tend to buckle up, while the pyrrole rings B and D tend to buckle down (Figure 4). The dihedral angles between the mean plane of the 24 core atoms and four phenyl groups 1–4 are 87.1, 77.7, 57.0, and 54.6°, respectively.

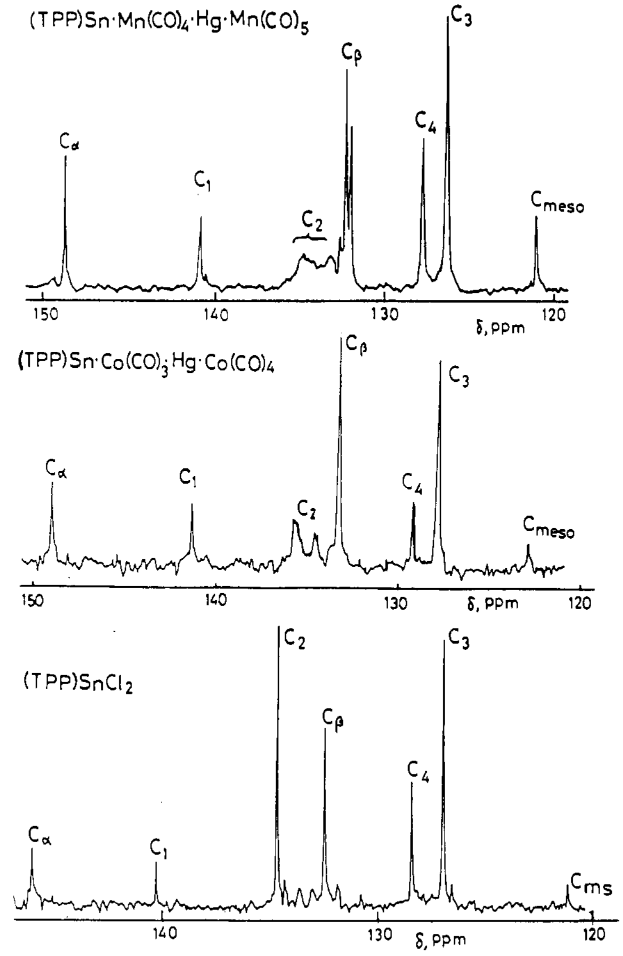

Figure 6. ^{13}C NMR spectra of **1**, **2**, and (TPP)$SnCl_2$ in $CDCl_3$ at room temperature.

Spectral Results. It is well established that the ortho phenyl protons are nonequivalent in ^1H NMR spectra for (*meso*-tetraphenylporphyrin)metal complexes in which the metal atom lies above the porphyrin plane or axial ligands coordinated to the central metal are nonequivalent.[25] For the present series of compounds, the central metal atom is five-coordinated and thus a similar phenomenon is expected. Figure 5 shows temperature-dependent ^1H NMR spectra for **1** and **2** in toluene-*d*. The broad peak observed at room temperature, which is assignable to ortho protons, splits into two peaks with a lowering of the temperature. In the (TPP)In–$M(CO)_n$ series of compounds, two ortho proton signals are observed even at room temperature.

Figure 6 displays ^{13}C NMR spectra of **1** and **2** in $CDCl_3$ at room temperature. The assignments of the ^{13}C NMR spectra were made with the aid of off-resonance mode and selective proton-decoupling mode measurements together with reference to the literature of the relevant porphyrin derivatives.[25] From the data in Table IV, it is found that α-pyrrole and meso carbon atoms are significantly influenced by the introduction of metal carbonyl groups in **1** and **2** compared to those of the parent (TPP)$SnCl_2$. Another interesting observation is that the β-pyrrole carbon

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[24] Indeed, our preliminary X-ray molecular structure analysis has shown that **2** has a linear four metal atom unit, Sn–Co(1)–Hg–Co(2), and the Sn–Co(1) bond length is shorter than regular tin–cobalt bond lengths: Onaka, S., to be submitted for publication.

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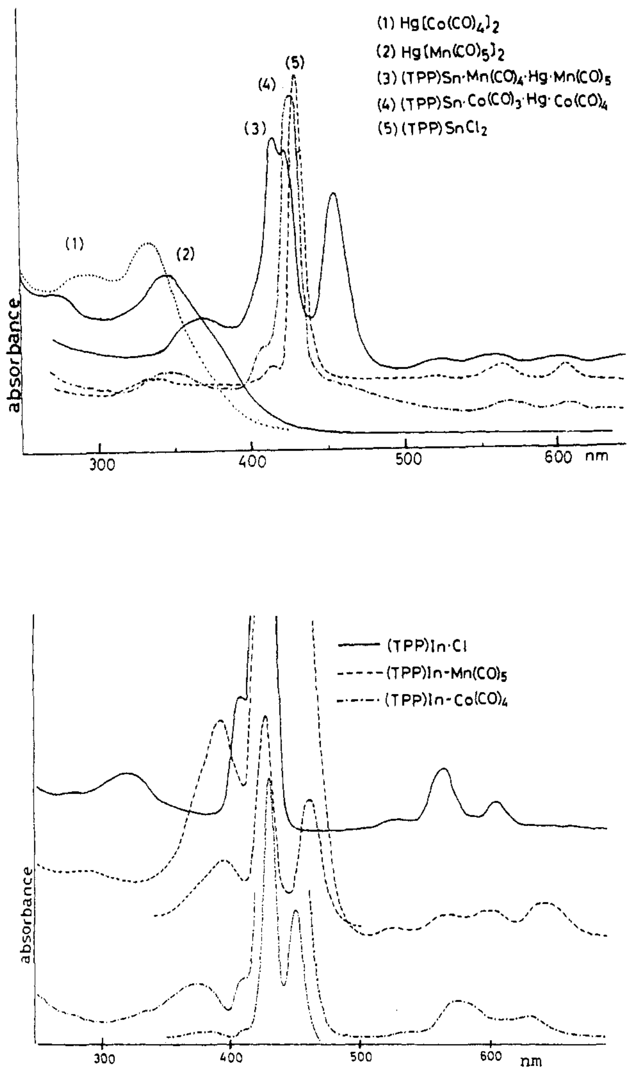

Figure 7. Absorption spectra in CH_2Cl_2 at room temperature.

resonance splits into two peaks in **1**. Presumably this splitting is caused by the fact that the magnetic effect that the β-pyrrole carbon atoms in the pyrrole ring B receives from the upper metal–metal bond framework is different from that of the β-pyrrole carbon atoms in other pyrrole rings. The single resonance of the β-pyrrole carbon atoms in **2** suggests that the Sn–Co(1)–Hg–Co(2) metal atom unit is linear.[24] In the indium porphyrin derivatives, the ortho carbon atoms are clearly split into two peaks at room temperature to suggest the presence of the indium–transition metal bond, while in **1** two broad peaks are detected for ortho carbon atoms at room temperature.

Figure 7 shows absorption spectra for **1–4** in CH_2Cl_2. A remarkable feature of the spectra is that a very strong absorption appears at around 450 nm in addition to the Soret band, and a broad shoulder is observed for **2** in this wavelength region. Another interesting feature of the spectra is that a fairly strong absorption appears in the 340–395-nm region by the construction of the metal–metal bond. As for the first feature, the relative intensity of the peak in the 400–500-nm region is sensitive to the solvent employed such as acetonitrile, isopropyl alcohol, benzene, and/or cyclohexane, and only one peak is observed in cyclohexane at around 450 nm for **1–6**. When the dichloromethane solutions were exposed to the fluorescent room light, the very strong absorption at around 450 nm and fairly strong absorption in the 340–395-nm region faded out gradually, the absorptions in the 560–660-nm region were blue shifted with isosbestic points, and finally the spectra were in complete agreement with those of (TPP)SnCl$_2$ and (TPP)InCl. The strong absorptions in the 340–395-nm region may be assigned to the $\sigma \rightarrow \sigma^*$ transition of the metal–metal bond concerned with each compound.[26,27] It is likely that the metal–metal bond is cleaved easily in CH_2Cl_2 under a fluorescent room light.[27,28] It is also certain that the upper metal carbonyl group(s) should have some responsibility for the appearance of the peak in the 450-nm region, although the exact interpretation of whether this peak is a split Soret band or this peak reflects some other origin such as a charge-transfer band is open to the future study.

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Registry No. **1**, 94928-89-9; **2**, 94943-90-5; **3**, 94928-90-2; **4**, 94943-91-6; (TPP)Sn-Co(CO)$_3$-Cd-Co(CO)$_4$, 94928-91-3; (TPP)Sn-Co(CO)$_3$-Zn-Co(CO)$_4$, 94928-92-4; (TPP)In-Co(CO)$_3$P(OPh)$_3$, 94928-93-5; (TPP)In-Re(CO)$_5$, 94928-94-6; (TPP)SnCl$_2$, 26334-85-0; Hg[Mn(CO)$_5$]$_2$, 15525-07-2; Hg[Co(CO)$_4$]$_2$, 13964-88-0; Mn$_2$(CO)$_{10}$, 10170-69-1; (TPP)InCl, 15525-07-2; Co$_2$(CO)$_8$, 10210-68-1; Cd[Co(CO)$_4$]$_2$, 16986-00-8; Zn[Co(CO)$_4$]$_2$, 16985-99-2; [Co(CO)$_3$P(OPh)$_3$]$_2$, 21118-36-5; Re$_2$(CO)$_{10}$, 14285-68-8; (TPP)InCl, 63128-70-1; Fe$_2$(CO)$_9$, 15321-51-4; Fe$_3$(CO)$_{12}$, 17685-52-8; Sn, 7440-31-5: Hg, 7439-97-6; In, 7440-74-6; Cd, 7440-43-9; Zn, 7440-66-6; Mn, 7439-96-5; Co, 7440-48-4; Re, 7440-15-5.

Supplementary Material Available: A stereoview of the unit cell contents (Figure 1) and listings of the phenyl C–C distances and angles, anisotropic thermal parameters, and observed and calculated structure factor amplitudes (59 pages). Ordering information is given on any current masthead page.

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