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Metal–Metal Bonds Extended Over a Porphyrin Ring.
II.* Resonance Raman and Far-infrared Spectra of Metalloporphyrins Containing In–M Bonds

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Abstract

The low-frequency resonance Raman (RR) and far-IR spectra of (TPP)In–M(CO)$_3$Cp (M = Mo and W) are reported. The ν(In–M) vibrations were located at ~160 and 147 cm^{-1}, respectively, for the Mo and W compounds. The RR excitation profiles were used to distinguish ν(In–M) from TPP vibrations which dominate the low-frequency spectra and to demonstrate that the split component of the Soret transition near 460 nm contains some σ(In–M)–σ^*(In–M) character.

Introduction

Since the presence of the metal–metal interaction in Fe$_2$(CO)$_9$ was first suggested in 1939 [2], a number of compounds containing metal–metal bonds have been synthesized and their structures and bonding studied using a variety of physicochemical methods [3, 4]. It has been found that the strength of the metal–metal bond varies widely from a typical single to quadrupole bond, depending upon the nature of the metal and the ligand involved [5]. Most of these compounds contain CO, halogen, carboxylate and other relatively simple ligands. Recently, however, a new class of metal–metal bonded compounds containing porphyrin as ligands have been synthesized. In 1977, Setsune *et al.* prepared Rh$_2$(OEP)$_2$ in which the presence of an Rh–Rh bond was suggested [6, 7]. This was followed by Onaka *et al.* who first synthesized (TPP)Sn–Mn(CO)$_4$–Hg–Mn(CO)$_5$ (TPP = tetraphenylporphinato dianion) which contains a σ-bonded bent four metal atom array, Sn–Mn–Hg–Mn [8, 1] and then by Collman *et al.* who synthesized a series of Ru$_2$(por)$_2$ type complexes where por denotes TPP, OEP (octaethylporphinato dianion), and TTP (tetra-*p*-tolylporphinato dianion) [1, 10]. Since then, several reports on the synthesis and characterization of the types: (por)MM′L, (por)MM(por), and (por)MM′(por) have appeared (L = (CO)$_n$ or (CO)$_3$Cp) [11–16]. These compounds have attracted special attention not only because of their synthetic interest and biological significance but also because of their potential superconducting properties.

Thus far, only a few reports are available on indium–transition metal bonded complexes in which simple ligands such as halogens are coordinated to the indium atom [17–20]. Recently, Cocolios *et al.* [11], Onaka *et al.* [1] and Barbe *et al.* [12] prepared a series of (por)In–ML$_n$ type complexes where M is Co, Cr, Mo, W, Mn, and Re and L is CO or Cp(CO)$_3$. Very recently, Guilard *et al.* [21] prepared a number of In–M σ-bonded porphyrins of the type mentioned above by using a new synthetic method and reported their physicochemical properties. The recent rapid increase of examples of In–M σ-bonded complexes indicates that porphyrins are excellent ligands to facilitate the formation of the In–M bond under mild conditions. In view of our earlier studies on (TPP)Sn–M(CO)$_{n-1}$–M′–M(CO)$_n$, (TPP)In–M(CO)$_n$, and (TPP)In–M(CO)$_3$Cp [8, 1], we have become interested in complete spectroscopic characterization of these complexes especially those containing In–M bonds. In our preliminary communication, we reported for the first time the ν(In–M) frequencies of the (TPP)In–M(CO)$_3$Cp series determined by FT-IR and resonance Raman (RR) spectroscopies [22]. The main purpose of this paper is to provide detailed discussions of our procedures which led to these assignments.

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*For Part I, see ref. 1.

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TABLE I. Electronic Absorption Spectra Data[a]

Compound	Medium		Soret region		α and β region		
(TPP)InCl	CH_2Cl_2		402(sh) 424(s)		558(vw)	597(vw)	
(TPP)In–Mo(CO)$_3$Cp	C_6H_{12}	380(m)	424(sh)[b]	456(s)	540(vw)	586(vw)	631(w)
	nujol	381(m)	427(sh)[b]	457(s)	544(vw)	587(vw)	631(w)
(TPP)In–W(CO)$_3$Cp	C_6H_{12}	369(m)	424(sh)[b]	453(s)	538(vw)		631(vw)

[a] λ_{max} (nm); sh, shoulder; vw, very weak; w, weak; m, medium; s, strong. [b] Bands due to $\pi \rightarrow \pi^*$ transition of the (TPP)In cation.

Experimental

Compounds

(Tetraphenylporphinato)indium(III) chloride, (TPP)InCl, was prepared according to the literature method [24]. (TPP)In–Cr(CO)$_3$Cp, (TPP)In–Mo(CO)$_3$Cp and (TPP)In–W(CO)$_3$Cp (Cp denoted the cyclopentadienyl group) were synthesized by using similar procedures reported previously [1, 14]. In general, the sample of [CpM(CO)$_3$]$_2$, where M is Cr, Mo or W, was dissolved in THF and stirred over 1% sodium amalgam at room temperature. After reaction was completed (formation of Na[CpM(CO)$_3$]), the supernatant was mixed with (TPP)InCl suspended in THF. The reaction was monitored by taking IR spectra in the carbonyl stretching region. Then THF was vacuum stripped and the residue was extracted with benzene. The solvent was completely distilled off in the vacuum and the first product was recrystallized from CH_2Cl_2–hexane or petroleum ether.

All the solvents: dichloromethane, hexane, cyclohexane, benzene, tetrahydrofuran (THF) and petroleum ether were purified and dried by standard procedures.

Spectral Measurements

The UV–Vis absorption spectra were recorded on a Perkin-Elmer model 320 spectrophotometer. Samples were dissolved either in cyclohexane or CH_2Cl_2 in the dark. The solid state (absorption and reflectance) spectra were measured for the samples dispersed in the Nujol and KBr discs, respectively. The results are collected in Table I. Far-infrared spectra were measured on an IBM IR/98 FT-IR spectrometer. The Nujol mull technique with polyethylene windows was used. The results are shown in Table II.

Resonance Raman spectra were recorded on a Spex 1403 double monochromator equipped with a Spex DM1B computer. Excitation lines were obtained from a Spectra-Physics Model 164-01 Kr-ion laser (406.7 and 568.2 nm), a Spectra-Physics Model 2020 Ar-ion laser (457.9; 465.8; 472.7; 476.5; 488.0 and 514.5 nm), and from a Liconix Model 4240 NB He–Cd laser (441.6 nm). The accuracy of frequency readings was ±1.0 cm^{-1}. The spectra were measured in the range from 500 to 100 cm^{-1}. The results are summarized in Table II. In a typical experiment, 1.0 mg of the sample and 80.0 mg of KBr were homogeneously mixed and then pressed to form a KBr pellet of 0.2 mm thick. A small portion (3 X 3 mm) of the KBr pellet thus prepared was attached to the copper cold tip cooled to ~20 K by a CTI Model 21 closed cycle helium refrigerator. This cooling together with the use of low laser power prevented thermal and/or photochemical decomposition of the sample. For excitation profile studies, 40.0 mg of PbO (internal standard) was homogeneously mixed with a few milligrams of the sample and 40.0 mg of KBr, and then pressed to form a pellet.

Results and Discussion

Electronic Spectra

Table I lists the electronic absorption maxima of (TPP)InCl in CH_2Cl_2; it exhibits weak α and β bands at 597 and 558 nm, respectively, and a strong Soret band at 424 nm accompanied by a weak shoulder at 402 nm. This is a typical 'normal porphyrin spectrum' defined by Gouterman [24]. When the chloride ion of (TPP)InCl is replaced by the M(CO)$_3$Cp group, which is attached to the In atom via σ-bonding, the Soret band splits into two components; one component shifts to the red (~460 nm) while the other component shifts to the blue (~380 nm). These spectra are typical of 'hyper' porphyrins [24].

Previously, Onaka *et al.* [1] suggested that the bands at 395–375 nm of (TPP)In–M(CO)$_n$ (M = Mn, Re or Co) and (TPP)Sn–M(CO)$_{n-1}$–M′–M(CO)$_n$ may originate in the $\sigma \rightarrow \sigma^*$ transition of the In–M bond [25, 26]. Although the nature of the second bands near 460 nm was not known, they observed that both bands disappear and a strong band emerges at 425 nm when the CH_2Cl_2

TABLE II. Low-frequency Spectra (cm^{-1}) of (TPP)InCl and (TPP)In–$M(CO)_3Cp$

(TPP)InCl		(TPP)In–$Mo(CO)_3Cp$		(TPP)In–$W(CO)_3Cp$		Band assignment
IR	RR	IR	RR	IR	RR	
		162	160	147	147	ν(In–M)[c]
182	184*	182	*	182	*	$\nu(C_m$–Ph), ν(In–M)
	194	194	194[a]	194	194[a]	
	203		202		202	
236		236		237		δ(por), ν(In–N), ν(In–M)
		248	244[a]	247	243[a]	
	252	264	262	264		
318		318[b]				$\delta(C_mC_\alpha N)$, $\nu(C_mC_\alpha)$, ν(In–N), ν(In–M)
	328		328		328	
	340	338	340	335	340	
		383	383[a]	381	384[a]	
396	401	397	401	393	400	$\delta(C_mC_\alpha N)$, $(C_\alpha C_m C_\alpha)$
433		431		428		
	445		438		451	γ(ring), δ(por)
478		474	476	474	476	
		482				
			495	492	496	

Abbreviations: ν = stretching, δ = bending, α = folding, C_m = methine bridge carbon, C_α, C_β = pyrrole carbons, Ph = phenyl Starred item: this band at ~185 cm^{-1} is hidden under 194 cm^{-1} band. [a]The ν(In–M) makes a particularly substantial contribution. [b]Due to traces of (TPP)In cation. [c]The ν(In–Cr) is observed at 172 cm^{-1} (IR) and 175 cm^{-1} (RR).

solution is exposed to fluorescent room light, and that the final spectrum becomes that of (TPP)$SnCl_2$ or (TPP)$InCl_2$ [1]. These results suggested that both bands should originate in the Sn–M or In–M linkages. Very recently Guilard *et al.* [21] reported that the bands near 460 nm of (TPP)In–$M(CO)_3Cp$ involve a porphyrin π–π^* transition while the bands near 380 nm of these compounds originate in a metal to porphyrin charge-transfer transition.

Resonance Raman and Far-IR Spectra

According to X-ray analysis, the Ru–Ru distance in $Ru_2(OEP)_2$ is 2.408 Å for which a formal M–M double bond has been assigned [9]. However, the In–M bond in (OEP)In–Rh(OEP) is much longer (2.584 Å) and regarded as a single bond [27]. The M–M′ linkages in (TPP)Sn–$Mn(CO)_4$–Hg–Mn(CO) [8, 1] and (OEP)Sn–$Fe(CO)_4$ [12] are also regarded as single bonds since their M–M distances are ~2.6 Å. Single bonded ν(M–M′) vibrations are known to appear below 250 cm^{-1} if M and M′ belong to the second and third rows of the periodic table [5, 28]. It is, therefore, reasonable to expect the ν(In–M) vibrations of the (TPP)In–$M(CO)_nCp$ type compounds below 250 cm^{-1}. Since the $[MCp(CO)_3]^-$ ions (M = Cr, Mo and W) [29] exhibit the ν(M–Cp) and δ(Cp) vibrations in the 319–299 and 353–335 cm^{-1} regions, respectively, the spectra below 300 cm^{-1} are largely due to TPP, ν(In–M) and their mixed modes. It is not simple, however, to distinguish these vibrations because their IR spectra are rather complex and their RR spectra are dominated by TPP vibrations when the excitation is made in the Soret region. Although the ν(In–M) vibrations can be assigned directly by the use of metal isotopes [30], it was not possible to apply this method to the present work since these compounds were difficult to prepare on a milligram scale.

Figure 1 shows the RR spectra of (TPP)In–Mo$(CO)_3Cp$ obtained by using four different exciting lines. The bands marked by asterisks are due to the internal standard (PbO) to which the intensities of individual bands compared. It is immediately seen that the intensities of the bands at 401 and 194 cm^{-1} are most sensitive to the exciting laser wavelength used; the former becomes strongest with 441.6 nm excitation (trace B) while the latter is maximized near 465 nm (trace C). This result suggests that the origins of resonance enhancement are markedly different for these two bands. Figure 1 shows, however, that the intensities of other bands at 384, 340, 244, 202 and 160 cm^{-1} also depend upon the laser wavelength used. The excitation profiles of all these (bands at 401, 340, and 202 cm^{-1}) and B-type which (TPP)In–$Mo(CO)_3Cp$ are plotted in Fig. 2.

Figure 2 shows two types of excitation profiles; A-type which exhibits a single maximum near 441 nm (bands at 401, 340 and 202 cm^{-1}) and B-type which exhibits a single maximum around 465 nm (bands at 384, 244, 194 and 160 cm^{-1}). Figure 3 compares

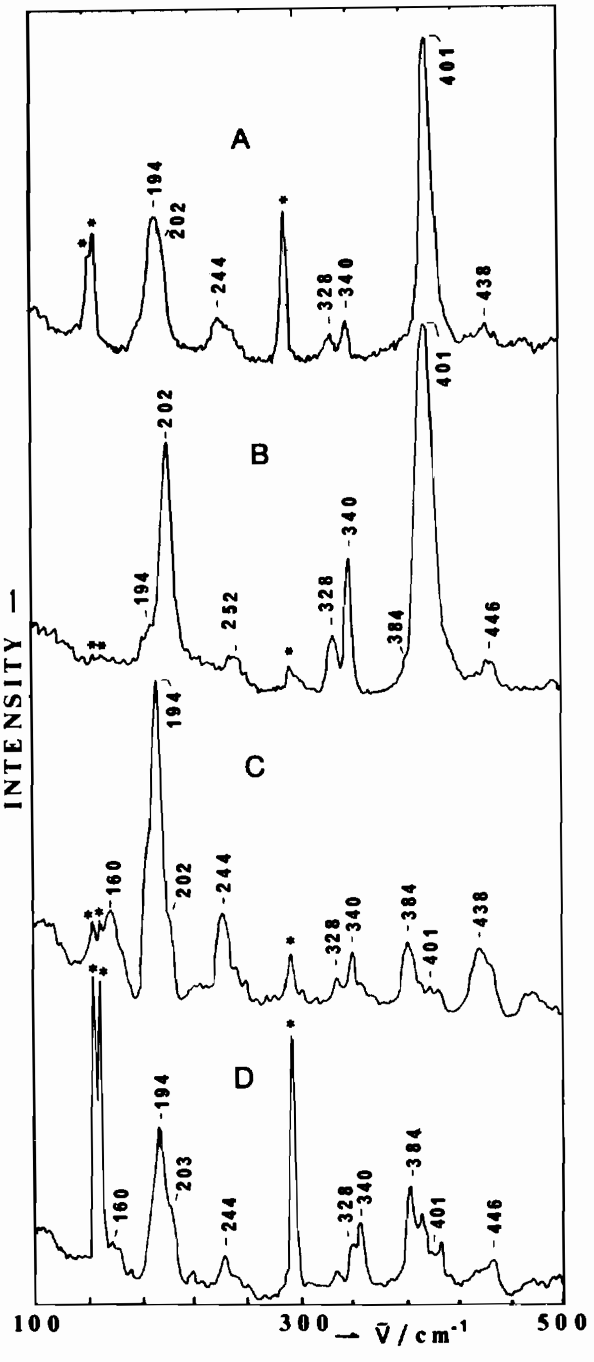

Fig. 1. RR spectra of (TPP)In–Mo(CO)$_3$Cp with excitation at 406.7 (A), 441.6 (B), 472.5 (C) and 488.0 (D) nm (KBr pellet).

the RR spectrum (457.9 nm excitation) of (TPP)InCl (trace A) with those of (TPP)In–Mo(CO)$_3$Cp (trace B) and (TPP)In–W(CO)$_3$Cp (trace C). The bands at 401, 340, 328 and 202 cm^{-1} of (TPP)InCl must be assigned to the (TPP)In moiety since it does not contain the In–M bond. Thus, A-type excitation profile suggests that these vibrations originate in the (TPP)In moiety.

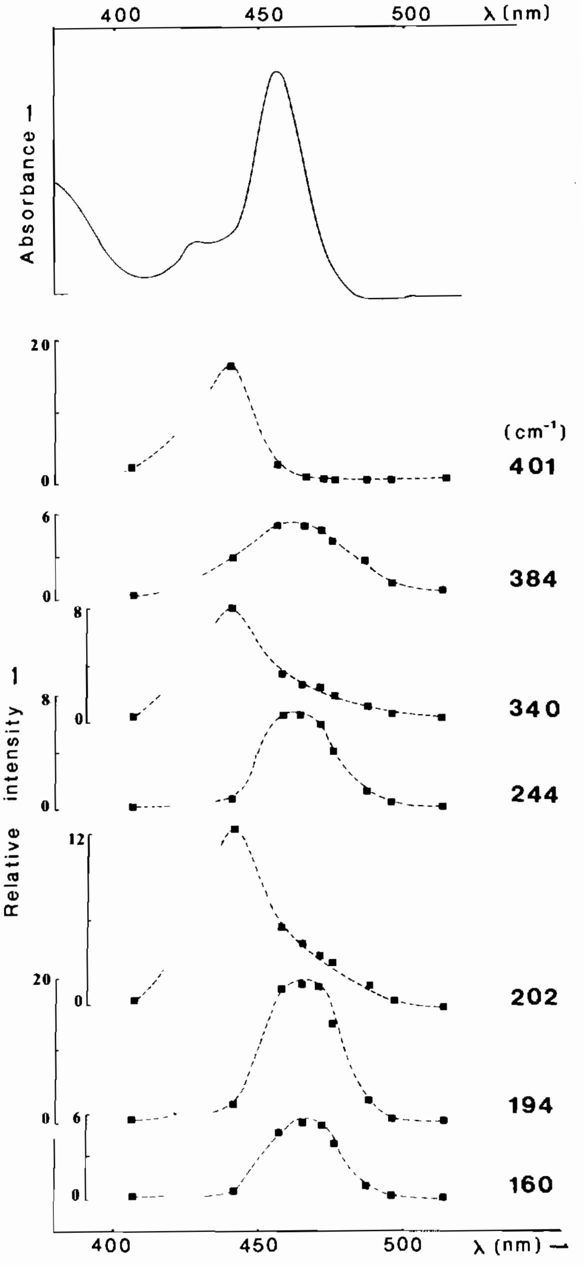

Fig. 2. Electronic absorption spectrum (Nujol) and excitation profiles of (TPP)In–Mo(CO)$_3$Cp. Exciting wavelengths are shown by solid square boxes.

Figure 4 compares the far-IR spectra of (TPP)InCl with that of (TPP)In–M(CO)$_3$Cp (M = Mo and W). It is seen that (TPP)In–Mo(CO)$_3$Cp exhibits bands at 162, 194, 248, 264 and 383 cm^{-1} which are not present in (TPP)InCl. The IR spectrum of the W compound is similar. The greater number of bands in (TPP)In–M(CO)$_3$Cp compounds arises from the lowering of symmetry in comparison with (TPP)InCl. The far-IR spectra combined with the RR excitation profiles suggest that these vibrations are

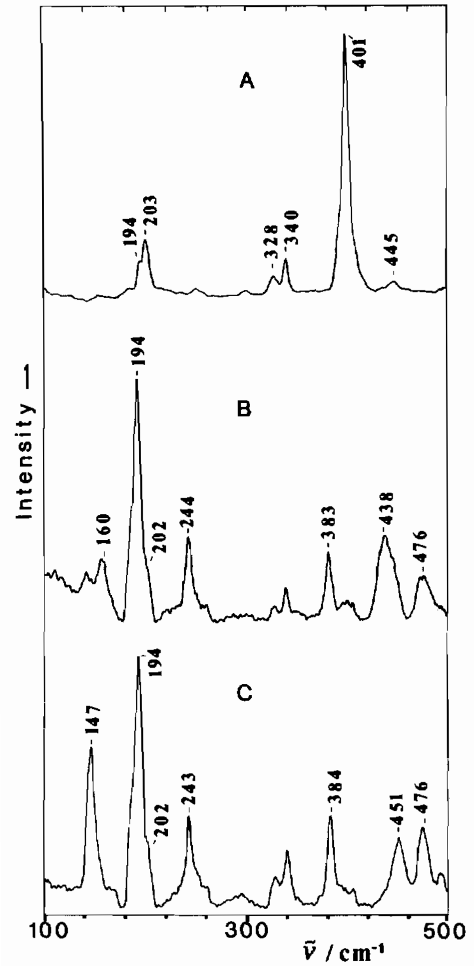

Fig. 3. RR spectra of (TPP)InCl (A), (TPP)In–Mo(CO)$_3$Cp (B) and (TPP)In–W(CO)$_3$Cp (C) at 457.9 nm excitation.

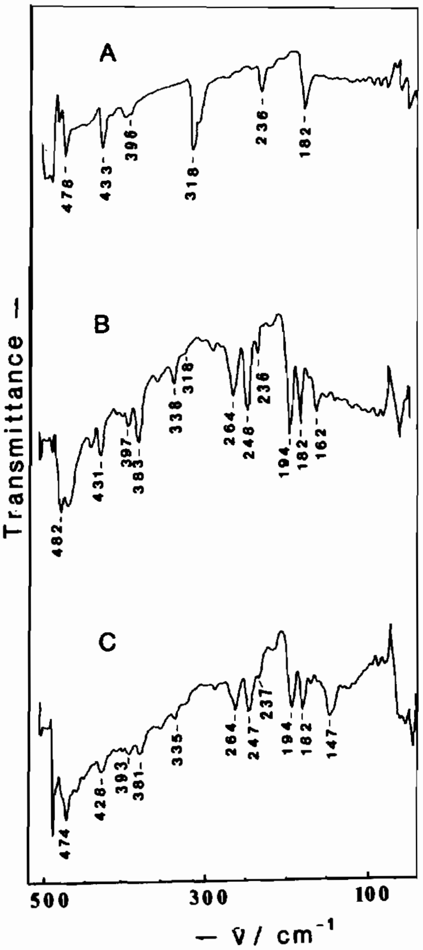

Fig. 4. Far-IR spectra of (TPP)InCl (A), (TPP)In–Mo(CO)$_3$-Cp (B) and (TPP)In–W(CO)$_3$Cp (C) in Nujol mulls.

due to the ν(In–M) or coupled modes between ν(In–M) and porphyrin skeletal modes.

As stated earlier, all the dimetallic compounds containing single M–M bonds are known to exhibit the ν(M–M) vibrations below 250 cm^{-1}. We have, therefore, focused our attention to the two vibrations at 194 and 162 ~ 147 cm^{-1} of (TPP)In–M(CO)$_3$Cp. As seen in Fig. 3, the band at 194 cm^{-1} is the strongest and most sensitive to the exciting laser wavelength among the B-type vibrations. However, this band cannot be assigned to the ν(In–M) since it is not sensitive to the change in metals. It is well known that the M–M bond becomes stronger as the mass of the metal increases in the same family of the periodic table [28]. Thus, in the [(CO)$_5$M–Re(CO)$_5$]$^-$ (M = Cr, Mo and W) series, the ν(Re–M) frequency decreases in the order of Cr (146 cm^{-1}) > Mo (130 cm^{-1}) > W (109 cm^{-1}) [31]. A similar trend is seen in the [(CO)$_5$M–Mn(CO)$_5$]$^-$ series [32]. The 194 cm^{-1} band is most likely due to deformation of the porphyrin core structure [33] with slight mixing of the ν(In–M).

As is seen in Fig. 4 and Table II, the far-IR spectra of (TPP)In–M(CO)$_3$Cp differ markedly in the region below 180 cm^{-1}; 162 (Mo) and 147 cm^{-1} (W). The corresponding RR bands are observed at 160 and 147 cm^{-1} (Fig. 3 and Table II). Thus, these bands are assigned to the ν(In–M) vibrations. The corresponding In–M stretching force constants are calculated to be 0.81 and 0.90 mdyn/Å, respectively, based on a simple diatomic oscillator assumption. Although we attempted to obtain the spectra of (TPP)In–Cr(CO)$_3$Cp in pure form, this was not possible because of contamination of (TPP)InCl impurity which resulted during the preparation and spectroscopic measurements. We noted, however, that a weak band near 173 cm^{-1} which does not appear in other compounds may be due to the ν(In–Cr) (the corresponding force constant, 0.63 mdyn/Å). The orders of these frequencies and force constants are in agreement with that observed previously for the [(CO)$_5$M–Re(CO)$_5$]$^-$ and [(CO)$_5$M–

$Mn(CO)_5]^-$ series [31, 32]. Thus, we assign these bands to a normal mode to which the ν(In–M) coordinate makes the major contribution.

It was noted, however, that the Raman intensity of the ν(In–M) is rather low although the exciting laser wavelength was chosen in a wide range. This result seems to indicate that any excitation in this region tends to cause strong enhancement of the porphyrin core vibrations since the In–M charge-transfer transition is mixed with the Soret π–π^* transition. The nature of other B-type vibrations at 384 and 244 cm^{-1} is not clear at this time. It is likely that these bands are due to porphyrin core deformation vibrations mixed with the ν(In–M). Table II lists the observed frequencies and most probable band assignments. These assignments were made based on previous RR [33–35] and IR [35, 36] studies on TPP complexes.

The In atoms in In(TPP)(CH_3) [37] and In(OEP)–Rh(OEP) [27] are displaced by 0.78 and 0.83 Å, respectively, from the plane of the four pyrrole nitrogens. Previously, Stong *et al.* [38] and Huong *et al.* [39] proposed equations which correlate the C_t–N distance (C_t: the center of the porphyrin core on the plane defined by the four pyrrole nitrogens (N)) with some porphyrin core vibrations in the high frequency region. In In(TPP)Cl and (TPP)In–W-$(CO)_3$Cp, the ν_3, ν_4 and ν_6 vibrations assigned by Stong *et al.* [38] are found at ~1552, ~1542 and ~1457 cm^{-1}, respectively. The ν_4 corresponds to ν_a of Huong *et al.* [39]. Using the equations and constants given by these workers, we have obtained the C_t–N distance of 1.99 Å from that of Stong *et al.*, and 2.09 Å from that of Huong *et al.* From these values, the In–C_t distance (out-of-plane deviation) is calculated to be 0.95 Å by the former and 0.72 Å by the latter. The In–C_t distances determined by X-ray analysis are between these two values (0.83–0.78 Å) as mentioned above. Thus, the equation by Stong *et al.* overestimates while that of Huong *et al.* underestimates the In–C_t distance.

As stated earlier, the nature of the two electronic transitions at ~380 and ~460 nm was not certain. Previously, Kadish *et al.* [14] assigned the two bands at 343 and 439 nm of (TPP)InCH_3 (in $CHCl_3$) to the 5p_z(In)–$e_g(\pi^*)$ and π–π^* transitions, respectively. These transitions may correspond to the bands at 380 and 456 nm of (TPP)In–Mo$(CO)_3$Cp observed in this work. Our RR studies described above strongly suggest that the Soret transition at 456 nm contains some σ(In–M′)–σ^*(In–M′) character.

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References

1 S. Onaka, Y. Kondo, M. Yamashita, Y. Tatematsu, Y. Kato, M. Goto and T. Ito, *Inorg. Chem., 24*, 1070 (1985).
2 H. M. Powell and R. V. G. Evans, *J. Chem. Soc.,* 286 (1939).
3 B. J. Bulkin and C. A. Rundell, *Coord. Chem. Rev., 2*, 371 (1967).
4 S. Onaka, T. Sugawara, Y. Kawada, Y. Yokoyoma and H. Iwamura, *Bull. Chem. Soc. Jpn., 59*, 309 (1986), and refs. therein.
5 K. Nakamoto, 'Infrared and Raman Spectra of Inorganic and Coordination Compounds', 4th edn., Wiley, New York, 1986.
6 J. Setsune, Z. Yoshida and H. Ogoshi, *J. Am. Chem. Soc., 99*, 3869 (1977).
7 J. Setsune, Z. Yoshida and H. Ogoshi, *J. Chem. Soc. Perkin Trans. I*, 983 (1982).
8 S. Onaka, Y. Kondo, K. Toriumi and T. Ito, *Chem. Lett.*, 1605 (1980).
9 J. Collman, C. E. Barnes, T. J. Collins, P. J. Brothers, J. Gallucci and J. A. Ibers, *J. Am. Chem. Soc., 103*, 7030 (1981).
10 J. P. Collman, C. E. Barnes, P. N. Swepston and J. A. Ibers, *J. Am. Chem. Soc., 106*, 3500 (1984); J. P. Collman, C. E. Barnes and L. K. Woo, *Proc. Natl. Acad. Sci. U.S.A., 80*, 7684 (1983).
11 P. Cocolios, C. Moise and R. Guilard, *J. Org. Met. Chem., 228*, C43 (1982).
12 J. M. Barbe, R. Guilard, C. Lecomte and R. Gerardin, *Polyhedron, 3*, 889 (1984).
13 K. J. Del Rossi and B. B. Wayland, *J. Chem. Soc., Chem. Commun.*, 1653 (1986).
14 K. M. Kadish, C. Swistak, B. Boisselier-Cocolios, J. M. Barbe and R. Guilard, *Inorg. Chem., 25*, 4336 (1986).
15 C. H. Yang, S. J. Dzugan and V. L. Goedken, *J. Chem. Soc., Chem. Commun.*, 1313 (1986).
16 J. P. Collman, K. Kim and J. M. Garner, *J. Chem. Soc. Chem. Commun.*, 1711 (1986).
17 P. D. Cradwick and D. Hall, *J. Organomet. Chem., 22*, 203 (1970).
18 D. J. Patmore and W. A. G. Graham, *Inorg. Chem., 5*, 1586 (1966).
19 J. M. Burlitch, M. E. Leonowicz, R. B. Peterson and R. E. Hughes, *Inorg. Chem., 18*, 1097 (1979).
20 H. J. Haupt, W. Wolfes and H. Preut, *Inorg. Chem., 15*, 2920 (1976).
21 R. Guilard, P. Mitaine, C. Moise, C. Lecomte, A. Boukhris, C. Swistak, A. Tabard, D. Lacombe, J. L. Cornillon and K. M. Kadish, *Inorg. Chem., 26*, 2467 (1987).
22 Y. Kato, L. M. Proniewicz, S. Onaka and K. Nakamoto, Paper presented at *Ann. Meeting Chem. Soc.*, Kyoto, Japan, April 1986.
23 M. Bhatti, W. Bhatti and E. Mast, *Inorg. Nucl. Chem. Lett., 8*, 133 (1972).
24 M. Gouterman, in D. Dolphin (ed.), 'The Porphyrins', Vol III, Academic Press, New York, 1978, Chap. 1.

25 R. A. Levenson, H. B. Gray and G. P. Caesar, *J. Am. Chem. Soc., 92*, 3653 (1970); R. A. Levenson and H. B. Gray, *J. Am. Chem. Soc., 97*, 6042 (1975).

26 S. Onaka, Y. Kondo, N. Furuichi, K. Toriumi and T. Ito, *Bull. Chem. Soc. Jpn., 56*, 87 (1983).

27 N. L. Jones, P. J. Carroll and B. B. Wayland, *Organometallics, 5*, 33 (1986).

28 D. F. Shriver and C. B. Cooper III, 'Vibrational spectroscopy of metal–metal bonded transition metal compounds', in R. H. J. Clark and R. E. Hester (eds.), 'Advances in Infrared and Raman Spectroscopy', Vol. 6, Heyden, London, 1980, p. 127.

29 R. Feld, E. Hellner, A. Klopsh and K. Dehnicke, *Z. Anorg. Allg. Chem., 442*, 173 (1978).

30 C. B. Cooper III, S. Onaka, D. F. Shriver, L. Daniels, R. L. Hance, B. Hutchinson and R. Shipley, *Inorg. Chim. Acta, 24*, L92 (1977).

31 J. R. L. Johnson, D. M. Duggan and W. M. Risen, *Inorg. Chem., 14*, 1053 (1975).

32 J. R. Johnson, R. J. Ziegler and W. M. Risen, *Inorg. Chem., 12*, 2349 (1973).

33 P. Stein, A. Ulman and T. G. Spiro, *J. Phys. Chem., 88*, 369 (1984).

34 J. M. Burke, J. R. Kincaid and T. G. Spiro, *J. Am. Chem. Soc., 100*, 6077 (1978).

35 H. Oshio, T. Ama, T. Watanabe, J. Kincaid and K. Nakamoto, *Spectrochim. Acta, Part A, 40*, 863 (1984).

36 J. Kincaid and K. Nakamoto, *J. Inorg. Nucl. Chem., 37*, 85 (1975).

37 C. Lecomte, J. Protas, P. Cocolios and R. Guilard, *Acta Crystallogr., Sect. B, 36*, 2769 (1980).

38 J. D. Stong, T. G. Spiro, R. J. Kubaska and S. I. Shupack, *J. Raman Spectrosc., 9*, 312 (1980).

39 P. V. Huong and J.-C. Pommier, *C. R. Acad. Sci. Paris, 285*, Series C, 519 (1977).