

## TRICARBONYLCHROMIUM $\pi$ -COMPLEXES OF ZN(II) TETRA (P-SUBSTITUTED PHENYL) PORPHIN

ZAHIR U. SIDDIQUI AND LOKE A. SUAN\*

*Department of Chemistry, University of Karachi, Karachi-75270, Pakistan*

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Tricarbonylchromium  $\pi$ -complexes of some Zn(II) tetra (p-substituted phenyl) porphin have been prepared by interacting hexacarbonyl chromium and Zn(II) tetra (p-substituted phenyl) porphin. Infrared spectra of these complexes in carbonyl stretching region shows two strong bands indicating a local  $C_{3v}$  point group symmetry. Visible spectra displays a shift toward higher wavelength in bands of Zn(II) tetra (p-substituted phenyl) porphin on addition of  $Cr(CO)_3$  group. No exchange of electron density between peripheral substituted phenyls seems to occur via porphin system in these complexes. An improved technique of preparation is developed and used to prepare these complexes. In this technique there is minimum loss of hexacarbonylchromium due to sublimation and no nitrogen gas pressure adjustments required after short intervals.

**Key words:** Tricarbonyl-porphin complexes.

### Introduction

Synthetic metal-chelates of porphins are an important class of compounds because they are structurally related to biological substances like heme, vitamin B<sub>12</sub> and chlorophyll. Substituted porphin metal-chelates have been thoroughly studied using IR, UV and visible, NMR, ESR spectroscopy and X-ray methods, these have been described in an earlier publication [1,12].

We studied metal-metal interaction and electron distribution in tricarbonylchromium  $\pi$ -complexes of transition metal tetraphenylporphin [M(II)TPPCr(CO)<sub>3</sub>] [1]. The interaction between metals was insignificant and we discovered that the peripheral benzene rings were not conjugated with porphin base. Conjugation of peripheral phenyls with the porphin  $\pi$  system was used to explain in part increase in intensity of visible band (Q(O-O) in Zn(II) tetra-(p-substituted phenyl) porphin [Zn(II)PXTTPP] by Longo and Quimby [2]. In tricarbonylchromium  $\pi$ -complexes of Zn(II) tetra[p-X(X = CH<sub>3</sub>, Cl, Br) phenyl] porphin [Zn(II)PXTPPCr(CO)<sub>3</sub>] the interaction between peripheral phenyl and porphin  $\pi$  system is studied by carbonyl stretching vibrations in the infrared region. Less than expected shift in  $\nu_{CO}$  indicates that electronic effects are not transferred from peripheral benzene to porphin  $\pi$  system. It is difficult to suggest on the basis of  $\nu_{CO}$  that peripheral benzene is somewhat distorted from a perpendicular position in these complexes. Although this distortion is necessary to explain increase in intensity of some visible bands by conjugation.

We studied earlier tricarbonylchromium  $\pi$ -complexes of metal Schiff bases where the benzene ring was an integral part of the conjugated system. The  $\nu_{CO}$  in the IR region

increased in the N- methyl-salicylalminato M-Cr(CO)<sub>3</sub> complexes with the number of d electrons in M. This trend was not observed in N-phenyl- salicylalminato M-Cr(CO)<sub>3</sub>[3].

### Experimental

**General.** UV-Vis spectra (CHCl<sub>3</sub>) were recorded on Hitachi 2000 or Cary 14 recording spectrometer and IR spectra (CHCl<sub>3</sub>) on 20-A Beckman or Perkin Elmer 475 spectrometer. Spectroscopic grade CHCl<sub>3</sub> was dried by molecular sieves and flushed with nitrogen gas before use. IR and UV-Vis cells and the sample were flushed with nitrogen gas before running the spectrum. If proper care was not taken the complexes decomposed.

**Preparation of tetra(p-substituted phenyl)porphin.** Tetra (p-methylphenyl) porphin [PCH<sub>3</sub>TTPP], [PC1TTPP], [PBrTTPP] were prepared by method of Adler *et al.* [4] by refluxing pyrrole and para-substituted benzaldehyde in propionic acid. They were purified by column chromatography using neutral alumina and chloroform. The visible spectra agreed with the reported spectra [5,6].

**Preparation of Zn(II) tetra (p-substituted phenyl)porphin.** The method of Adler *et al.* [7] was used to prepare zinc derivatives by refluxing PCH<sub>3</sub>TTPP, PC1TTPP, and PBrTTPP separately with a four fold molar excess of ZnCl<sub>2</sub> in boiling dimethyl formamide. The zinc derivatives were recrystallized from toluene-methanol and dried under vacuum. TLC showed that the three compounds were pure. The visible spectra agreed with the recorded spectra [2].

**Reaction of Cr(CO)<sub>6</sub> with Zn(II)PCH<sub>3</sub> TPP.** Cr(CO)<sub>6</sub> [0.005 mol] was refluxed with Zn(II) PCH<sub>3</sub> TPP [0.001 mol] in 300 ml of peroxide free and sodium dried di-n-butyl ether in an atmosphere of nitrogen as shown in Fig. 1. The solvent

\*University Science Malaysia, Penang, Malaysia.



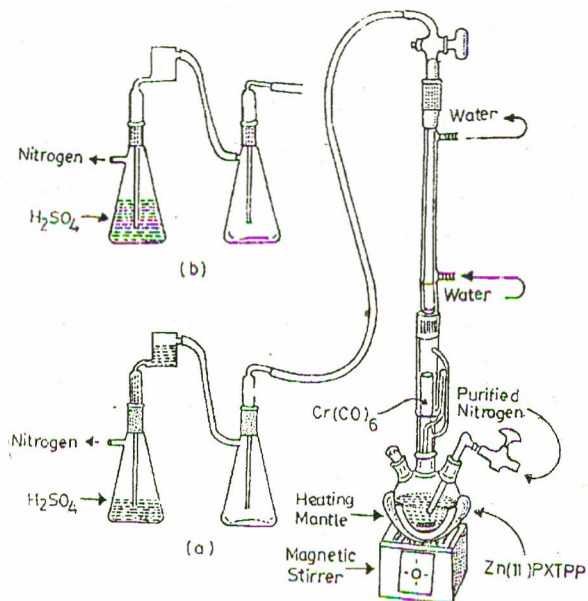


Fig. 1. Apparatus for the preparation of (a)  $\text{H}_2\text{SO}_4$  sucked back into extra construction (b)  $\text{H}_2\text{SO}_4$  back to the original flask.

and the unreacted  $\text{Cr}(\text{CO})_6$  were removed after carrying the reaction for six hrs by vacuum evaporator. The vacuum dried solid product was chromatographed on Florisil and  $\text{Zn}(\text{II})\text{PCH}_3\text{TPPCr}(\text{CO})_3$  was recovered as second fraction. First fraction was  $\text{Zn}(\text{II})\text{PCH}_3\text{TPP}$  and third was a decomposed complex as it did not show any carbonyl bands.  $\text{Zn}(\text{II})\text{P-CH}_3\text{TPPCr}(\text{CO})_3 \cdot 2\text{H}_2\text{O}$ ; yield 29%. anal. calc. for  $\text{C}_{51}\text{H}_{40}\text{N}_4\text{O}_5\text{CrZn}$ : C, 67.62; H, 4.41; N, 6.18. found: C, 67.18; H, 4.48; N, 6.15%.

**Reaction of  $\text{Cr}(\text{CO})_6$  with  $\text{Zn}(\text{II})\text{PCITPP}$  and  $\text{Zn}(\text{II})\text{PBrTPP}$ .** The reaction was carried out as described for  $\text{Zn}(\text{II})\text{PCH}_3\text{TPP}$ . Both the solid products were run through a Florisil column and the second fraction was the tricarbonylchromium complex in each case.  $\text{Zn}(\text{II})\text{P-CITPPCr}(\text{CO})_3 \cdot 2\text{H}_2\text{O}$ ; yield 34%. Anal. Calc. for  $\text{C}_{47}\text{H}_{28}\text{N}_4\text{O}_5\text{CrZn}$ : C, 57.13; H, 2.83; N, 5.67. Found: C, 56.92; H, 2.87; N, 5.63%.  $\text{Zn}(\text{II})\text{P-BrTPPCr}(\text{CO})_3 \cdot 2\text{H}_2\text{O}$ ; yield 31%. anal. calc. for  $\text{C}_{47}\text{H}_{28}\text{N}_4\text{O}_5\text{CrZn}$ : C, 43.55; H, 2.16; N, 4.32. found: C, 43.12; H, 2.21; N, 4.34%.

**Improved technique.** All earlier methods of open system [8-10] used a continuous flow of nitrogen. If a high rate of flow of nitrogen was used then most of the  $\text{Cr}(\text{CO})_6$  accumulates inside the water condenser and it becomes a problem to bring it back to reaction flask. On the other hand if a very slow rate of flow was maintained then the solvent started to enter the tube by which the nitrogen gas was entering the reaction flask. Therefore it becomes necessary to watch the rate of flow of nitrogen at intervals to maintain a medium rate of flow. The  $\text{H}_2\text{SO}_4$  in the exit flask was sucked back in the nalgon tubing when solvent started to return from Soxhlet to reaction flask.

The back suction of  $\text{H}_2\text{SO}_4$  can be stopped by increasing the rate of flow of nitrogen but this removed most of  $\text{Cr}(\text{CO})_6$  to condenser. To overcome these problems, construction of a glass cylinder as shown in Fig. 1a was made on the flash containing the  $\text{H}_2\text{SO}_4$ . Once the inert atmosphere was created the valve by which nitrogen gas entered reaction flask was closed. Since there was no flow of nitrogen, the loss of  $\text{Cr}(\text{CO})_6$  due to sublimation was minimum. The back suction became operative when solvent started to go back to reaction flask from Soxhlet and as a result  $\text{H}_2\text{SO}_4$  was sucked back into extra construction (Fig. 1a). When solvent starts to enter Soxhlet from reaction flask,  $\text{H}_2\text{SO}_4$  starts to return to flask containing  $\text{H}_2\text{SO}_4$  (Fig. 1b).

## Results and Discussion

**Synthesis and structure.** All the complexes prepared showed two strong bands in carbonyl stretching region and a change in the visible spectrum of  $\text{Zn}(\text{II})\text{PXTTPP}$  indicating the formation of tricarbonylchromium complexes of  $\text{Zn}(\text{II})\text{PXTTPP}$ . The structure (Fig. 2) of  $\text{Zn}(\text{II})\text{PXTTPPCr}(\text{CO})_3$  complexes is deduced by analogy to established structure of  $\text{Zn}(\text{II})\text{TPPCr}(\text{CO})_3$  [1].  $\text{Zn}(\text{II})\text{TPPCr}(\text{CO})_3$  and  $\text{Zn}(\text{II})\text{PXTTPPCr}(\text{CO})_3$  complexes have similar IR and visible structural features. In our previous work we isolated complexes of  $\text{Zn}(\text{II})\text{TPP}$  with one and two  $\text{Cr}(\text{CO})_3$  groups attached. Both complexes with one or two  $\text{Cr}(\text{CO})_3$  groups had similar position of CO stretching vibrations, but their visible spectra were slightly different [1].

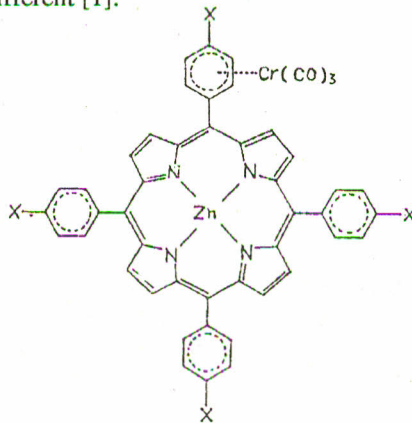


Fig. 2. Structure of the  $\text{Zn}(\text{II})\text{PXTTPPCr}(\text{CO})_3$  complexes, where  $\text{X}=\text{CH}_3$ , Cl, Br.

These complexes were very sensitive to air in solution therefore the whole process of purification by chromatography was carried out under nitrogen atmosphere. The eluent ( $\text{CHCl}_3$ ) was dried by molecular sieves. If the complexes purified by chromatography were left on column for long time they decomposed.

When  $\text{Zn}(\text{II})\text{PXTTPPCr}(\text{CO})_3$  complexes were completely decomposed the visible spectrum of  $\text{Zn}(\text{II})\text{PXTTPP}$  were



obtained. The solid complexes decomposed giving the parent compound Zn(II)PXTTPP on heating above 100°. A broad band at 3200-3600 cm<sup>-1</sup> indicates presence of H<sub>2</sub>O in these complexes. All the efforts to record a NMR spectrum on HA-100 failed.

*Visible spectra.* According to four orbital model [11] the intensities of visible bands in porphins are determined by the degree of degeneracy of top filled orbitals b<sub>1</sub>(a<sub>2u</sub>) and b<sub>2</sub>(a<sub>1u</sub>). When the orbitals are exactly degenerate the Q(O-O) bands have zero intensity. With the removal of degeneracy of these orbitals the band intensity increases. The degeneracy can be removed due to conjugative and inductive interaction of phenyl rings and phenyl substituents with b<sub>1</sub>(a<sub>2u</sub>) orbital due to its suitable nodal property [11]. The intensity of Q(O-O) band increases in Zn(II)PXTTPPCr(CO)<sub>3</sub> complexes (Table 1). When Cr(CO)<sub>3</sub> groups are attached to Zn(II)PXTTPP, the absorption

TABLE 1. VISIBLE SPECTRA OF COMPLEXES, N.M. (ε × 10<sup>-3</sup>)

Complex	Q(0-0)	Q(1-0)	B(0-0)
Zn(II)PCH <sub>3</sub> TPP	588(3.72)	549(23.8)	424(540)
Zn(II)PCH <sub>3</sub> TPPCr(CO) <sub>3</sub>	600(4.10)	561(13.0)	426(207)
Zn(II)PC1TPP	589(3.92)	551(24.2)	424(555)
Zn(II)PC1TPPCr(CO) <sub>3</sub>	601(4.24)	562(13.3)	426(213)
Zn(II)PBrTPP	589(4.10)	551(24.2)	424(556)
Zn(II)PBrTPPCr(CO) <sub>3</sub>	602(4.38)	563(12.6)	426(214)

maxima in visible region for Zn(II)PXTTPP are shifted to higher wavelengths. The intensity of Q(1-0) and B(O-O) bands is decreased after the addition of Cr(CO)<sub>3</sub> groups. More extensive conjugative interaction was the explanation given in ortho-substituents Zn(II)OXTTPP for increased Q(O-O) band intensity [2]. In Zn(II)PXTTPPCr(CO)<sub>3</sub> band intensity increase compared to Zn(II)PXTTPP may be due to additional Cr(CO)<sub>3</sub> groups which may be increasing the conjugative interaction. A conjugative interaction does not seem probable if para-substituted benzene with Cr(CO)<sub>3</sub> group attached is assumed perpendicular to porphin base. X-ray studies have shown that phenyl rings are perpendicular to the plane of porphin system in Zn(II)TPP [12]. The intensity changes in the visible bands of these complexes suggest that there is some deviation of phenyl ring from perpendicular position.

*Infrared spectra.* We have used carbonyl stretching vibrations in infrared region to determine electron distribution and local symmetry of chromium carbonyl complexes of transition metal-chelates [1,3]. It has been shown [13,14] that CO stretching vibrations position increases if X is an electronegative molecule or ion and decreases if X is an electron donating molecule in XACr(CO)<sub>3</sub> complexes (XAr = benzene with substituents like CH<sub>3</sub>, Cl, F etc.). Looking at CO stretching

vibrations (Table 2) in these complexes we see a similar trend. The increase and decrease of CO stretching vibrations are in the ±5 cm<sup>-1</sup> range in these complexes. A higher shift was expected if para-substituted benzene was conjugated with porphin π system. In a similar situation electronic effects are

TABLE 2. INFRARED IN THE CO STRETCHING REGION.

Complex	cm <sup>-1</sup> (CHCl <sub>3</sub> )
Zn(II)TPPCr(CO) <sub>3</sub>	1902, 1972
Zn(II)PCH <sub>3</sub> TPPCr(CO) <sub>3</sub>	1898, 1966
Zn(II)PC1TPPCr(CO) <sub>3</sub>	1907, 1978
Zn(II)PBrTPPCr(CO) <sub>3</sub>	1905, 1976

transferred from CH<sub>3</sub> substituent to the adjoining ring in tricarbonylchromium complexes of substituted biphenyls. The ν<sub>CO</sub> decreased in 4,4-dimethylbiphenyl tricarbonylchromium complexes by 9 cm<sup>-1</sup> due to methyl substituents [15]. In Zn(II)PCH<sub>3</sub>TPPCr(CO)<sub>3</sub> the electronic effects were expected to be transferred due to three methyl substituents to the ring to which Cr(CO)<sub>3</sub> group is attached. The shift observed in ν<sub>CO</sub> is not expected of a conjugated system. However, the visible spectra suggest deviation from perpendicular position of -ArX(CO)<sub>3</sub> group to porphin system to explain the increase in intensity of visible bands due to conjugation. A partial departure from perpendicularity will be sufficient to change the intensities of the visible bands but insufficient to change the CO stretching vibrations.

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