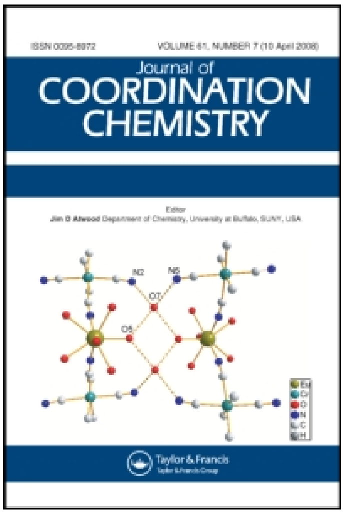

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STRUCTURAL CHARACTERIZATION OF BI-NUCLEAR COBALT(III) AXIAL-METHYL ALCOHOL-HYDROCHLORIC ACID TETRAPHENYL-PORPHYRIN COMPLEX

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STRUCTURAL CHARACTERIZATION OF BI-NUCLEAR COBALT(III) AXIAL-METHYL ALCOHOL-HYDROCHLORIC ACID TETRAPHENYL-PORPHYRIN COMPLEX

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Simple modification(s) of the conventional preparation of **Co(II)TPP** led to a new cobalt complex. Structural investigation of the new complex was carried-out by using elemental analysis, physicochemical and spectroscopic techniques. (1) The **EDXRF** spectrum indicates the presence of Cl^- in 1 : 1 ratio with the cobalt ion. (2) **IR** analysis indicates that; (i) No changes in the main aromatic moieties of the ligand **H_2TPP** after chelation. (ii) The cobalt-ion is sited in the porphyrin core. (iii) The oxygen of methyl alcohol is attached to a non-carbon atom. (iv) Cobalt–nitrogen bonds are coordinate bonds. (3) **UV** results show a **Co(III)** metal ion is significantly changed by the nature of the axial ligands with only one band at 1525 nm. The split Soret band at 1395 and 1411 nm without shoulders could ensure the axiality of $H-\underset{..}{\overset{..}{Cl}}$ and $(H-\underset{..}{O}-C\overset{..}{H}_3)$ as electron withdrawing ligands. (4) Measurement of the magnetic susceptibility indicates that +3 is the oxidation state of the central cobalt ion of the prepared complex. (5) **TGA** analysis ensured that one **Co(III)** ion is chelated with one **TPP^{2-}** dianion to produce one mole of complex. (6) **X-ray** diffraction analysis reveals that the main porphyrin core is preserved. However, due to metallation, the length of the Co–Co bond in a binuclear structure, *via* lateral overlap of d_π–d_π orbitals to achieve back-donation, is estimated as (3.06–3.22 Å). (7) **NMR** spectra of both **H_2TPP** and the prepared complex ensured removal of NH protons with characteristic bonds for both phenolic and pyrrolic protons. Although, the rotar protons of **H_3COH** appear upfield, the hydrochloric acid proton is assigned downfield. The number of protons detected by **NMR**, is in agreement with that predicted by elemental analysis. The final structure of the synthesized complex is predicted according to the C, H and N analysis as **$C_{45}H_{33}N_4$ OClCo** in a binuclear form. The above analysis indicates that the binuclear structure is dominant in the solid phase; the charged structure is preferred in solution.

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Keywords: Cobalt(III); porphyrins; suprabiotic catalyst; binuclear

INTRODUCTION

The porphyrin nucleus is a cyclic tetrapyrrolic system consisting of a 20-carbon skeleton, the four pyrroles are linked by single carbon atom bridges. The porphyrin macrocycle contains a total of 22π electrons with 18p electrons in direct conjugation. Porphyrins exhibit a characteristic intense absorption in the UV–visible spectrum near 400 nm, known as the Soret band. In addition, porphyrins exhibit four less intense visible bands between 450 and 700 nm. Based on the relative intensities of these four visible bands, four basic types of spectra named Etio, Rhodo, Oxorhodo and Phyllo have been observed. They have been interpreted by the electronic nature of the peripheral substituents based on the perturbations of π-electron levels.[1]

The tetradentate anionic porphyrinato ligand is generated by the loss of the two inner NH protons; almost all metal ions coordinate with it. In the synthesis of metalloporphyrins five essential stages must be justified.[2] However, metal ions with charges greater than 2^+ coordinate axial ligands to attain electroneutrality. The metallation process is optimally carried out in highly concentrated solutions.

Complexes of Co(III) are exceedingly numerous. All known discrete Co(III) complexes are octahedral, though tetrahedral and square-antiprismatic–Co(III) complexes are known in a few solid-state situations.[3] All known octahedral Co(III) complexes have diamagnetic, low spin ground states, with the exception of $[Co(H_2O)_3F_3]$ and $[CoF_6]^{3-}$ which are paramagnetic with four unpaired electrons.

Co(III) shows a particular affinity for nitrogen donors as well as halide ions. In general, Co(III) complexes are synthesized in a solution, *via* oxidation of Co(II) ions by oxygen or hydrogen peroxide. A similar oxidation process by HCl solution, produces Co(III) ion as a salt.[4,5]

Many Co(II) complexes such as $(Co(NH_3)_6^{2+})$, are readily oxidized to give conventional Co(III) complexes as products (*e.g.* $Co(NH_3)_6^{3+}$). There are interesting binuclear peroxo-bridged species, such as $[(NH_3)_5CoOOCo(NH_3)_5]^{4+}$ or $[(NC)_5CoOOCo(CN)_5]^{6-}$, that can be isolated in the absence of catalysts.[6] Similarly the well-characterized M–M bonded binuclear species, $[(NC)_5Co{-}Co(CN)_5]^{6-}$ can be precipitated by addition of KCN to an aqueous solution of Co(II).[7,8] The catalytic activity of Co–Co binuclear catalyst is much larger than for individual mono-metallic catalysts.[9] The best known biological function of cobalt is its intimate involvement in the coenzymes related to vitamin B_{12}.[10] The macrocyclic structure belongs to the corrin system, reminiscent of the porphyrin system, with the absence of a methine (CH) bridge between one pair of pyrrole rings. Finally, there are a number of model systems that consist of a rigid planar ligand system with the axial sites occupied by an anion that may be a carbanion and a halide anion.[11–13] The synthesis and characterization of cobalt tetraphenylporphyrin Co(II)TPP was extensively studied.[14–16] In addition, the catalytic activity of this complex, has been investigated by loading the complex on different supports (*e.g.* SiO_2, Al_2O_3 and TiO_2). Variation in electronic interactions between the complex and the support measured by UV and ESR have been investigated.[17–19] The catalytic activity of Co(II)TPP as electron donors and acceptor has been studied.[20–23]

It is expected that modifying the method(s) of preparation of the Co(II)TPP complex, previously described in literature, would only affect the complex yield. However, the catalyst exhibited higher catalytic activity, supported on different organic or inorganic carriers, when tested on the decomposition of H_2O_2.

The aim of the present work, is to thoroughly investigate the structure of the prepared catalyst, by physicochemical and spectroscopic techniques, in order to understand these extremely high catalytic activities. Full characterization of the prepared catalyst will be the subject of forthcoming paper(s).

EXPERIMENTAL

Tetraphenyl porphyrin (**H_2TPP**) was synthesized[24] to be used as a ligand. Simple modifications on the conventional preparation procedure of Co(II)TPP was achieved by gradual addition of an oxygenated saturated solution of anhydrous $CoCl_2$ in dry DMF to a mixture of recrystallized **H_2TPP** dissolved in dry DMF.[25] The mixture was exposed to 45 KHz ultrasonic frequencies at a temperature of 75°C with continuous stirring for 4 h. Distilled dry methanol was added to the vessel's contents and the formed crystalline precipitate was allowed to settle slowly for 24 h.

The percentages of C, H and N for the synthesized ligand and its prepared complex were determined by using an elemental analyzer Perkin-Elmer model 2400. The complex's structure was investigated by:

(A) Physicochemical techniques

1. TGA-Spectrometer, model Stanton-Redcroft with thermo-balance type 750/770 connected to a Kipp and Zonnen BDG two-channel automatic recorder.

(2) EDXRF-Link system joined with SEM model JOEL TSM T 2000.
(3) Magnetic balance model MKI was used to measure the magnetic-susceptibility.
(4) Electrolytic-conductance unit model YS132 with a platinum electrode YS132.
(5) XRD measurements by using an X-Ray Spectrodiffractometer model Philips 1979.

(B) Spectroscopic techniques

(1) IR and far-IR, PYE-Unicam spectrometer model 3-200sp.
(2) UV–visible spectrometer, Perkin-Elmer model Lambda 3B.
(3) Barker 200 MHz NMR spectrometer.

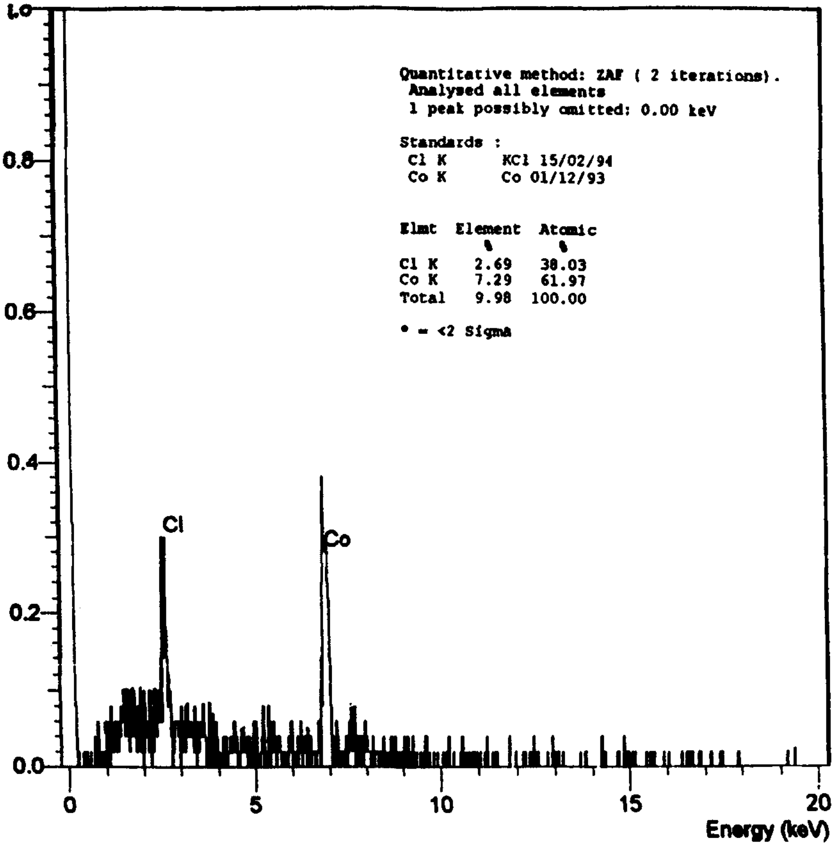
RESULTS AND DISCUSSION

Results

Figure 1 shows the EDXRF pattern of the synthesized complex. Two K_α peaks, characteristic for chlorine and cobalt atoms, with atomic percentages 38.03 and 61.97, respectively, show the ratio of Co and Cl in this complex is 1 : 1.

Table I includes the practical IR absorption bands of the ligand "**H_2TPP**" and its prepared complex within a frequency range 4000–200 cm^{-1}. The prominent absorption bands of the ligand, resemble those previously published.[26] However, the IR-spectrum of the complex exhibits three sets of characteristic metal-dependent bands. (i) The absorption assigned at ν3552 cm^{-1} is related to the Co–N bond.[27] (ii) The stretching bands at ν237 and ν219 cm^{-1} indicate a transition metal ion bound to a nitrogen atom involved in a conjugated system.[28–30] (iii) The appearance of a weak band at ν1174 cm^{-1} indicates the existence of a stretching bond between the oxygen of the methyl-alcohol $H{-}O{-}CH_3$ attached to the non-carbon system.[31] The weak absorption band at 1654 cm^{-1} is assigned to $-C{=}N-$ having double bond character while the band at 1349 cm^{-1} is related to the strong $-C{-}N$ stretch with considerable single bond properties.

Figure 2 shows the ultraviolet and visible absorption spectra of the ligand **H_2TPP** and the prepared complex in benzene. In the visible region, the absorption bands of the synthesized compounds are located within the range 430–668 nm. The high purity of the prepared ligand is shown by comparison to the bands previously published for the pure ligand.[32,33] However metallation reduced the number of bands to one main absorption band at 525 nm without shoulders. Disappearance of the three bands relative to the



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Quantitative method: ZAF ( 2 iterations).
 Analysed all elements
 1 peak possibly omitted: 0.00 keV

Standards :
 Cl K      KCl 15/02/94
 Co K      Co 01/12/93

Elmt  Element  Atomic
         %        %
Cl K    2.69    38.03
Co K    7.29    61.97
Total   9.98   100.00

* = <2 Sigma
```

FIGURE 1 The EDXRF pattern of the synthesized Co-TPP complex.

parent ligand is attributed to the interaction of the rearranged phenyl rings with the disturbed equatorial plane of the four pyrrolic nitrogen atoms.[34,35] In the near ultraviolet region, the ligand and its complex exhibit two similar, intense, characteristic split Soret bands at λ411 and 395 nm. However, disappearance of the shoulder at λ368 nm from the Soret band of the cobalt complex, indicates a decrease of the delocalized electronic densities over the porphyrin-core.

The magnetic susceptibility (ψ_m) and the effective magnetic moment (μ_{eff}) values are computed for the prepared complex according to the following equation:

$$\psi_m = C * L(R - R_0) * \mathrm{Mw/sample\ wt\ (g)} * 10^9,$$
$$\mu_{eff} = 2.4(\psi_m * T)^{0.5},$$

TABLE I IR absorption bands of both synthesized ligand (H_2TPP) and its corresponding Co-complex

No.	*IR digital spectra of the synthesized compounds*				*Remarks*
	Ligand H_2TPP		*CoTPP complex*		
	cm^{-1}	$\%T$	cm^{-1}	$\%T$	
1	—	—	3552	20	Ionic Co–N bond
2	—	—	1655	45	C=N have considerable double bond character
3	1597	27	—	—	
4	1489	31	—	—	
5	1439	26	1439	46	C–H pyrrolic bending vibrator
6	1344	18	1350	43	Non-hydrogen pyrrolic nitrogen –C=N having single bond properties
7	1205	37	—	—	
8	—	—	1174	37	H–O–CH_3 attached to non-carbon system*
9	1070	28	1072	50	Pyrrolic ring
10	1005	10	1005	38	C–H stretch band of pyrrol
11	833	41	835	53	Characteristic bands for TPP molecule as a whole
12	793	21	795	46	
13	741	23	741	46	
14	710	32	—	—	
15	696	20	698	43	Characteristic band for TPP molecule as a whole
16	658	43	—	—	
17	523	50	—	—	
18	444	49	—	—	
19	—	—	418	55	
20	280	36	—	—	
21	247	20	—	—	
22	—	—	237	12	General stretch bends for transition metal with unsaturated nitrogen in conjugated system coordinatively
23	214	6	220	20	
24	—	—	204	55	

*Oxygen methyl alcohol attached to a non-carbon system.

where, L and R have derived values 2.9 cm and –36 respectively and C and R_0 are empirical constants having values 1.0399 and –33, respectively.

The negative and imaginary values of ψ_m and μ_{eff}, imply the cobalt ion in the synthesized complex is diamagnetic. Therefore, the oxidation state +3 is favored for the cobalt ion.

Table II shows the data for the C, H and N elemental analysis for both **H_2TPP** and its cobalt complex. The concordance of the data with the calculated percentages of C, H and N for the pure ligand, indicates that the empirical formula $C_{44}H_{30}N_4$ corresponds to the chemical formula of **H_2TPP**. The found C, H and N percentages of the cobalt complex are in

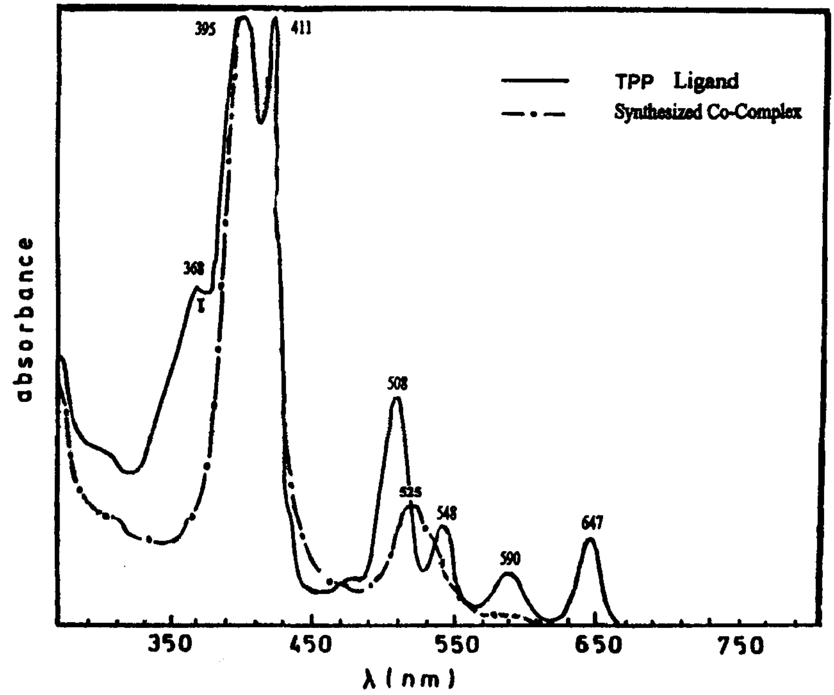


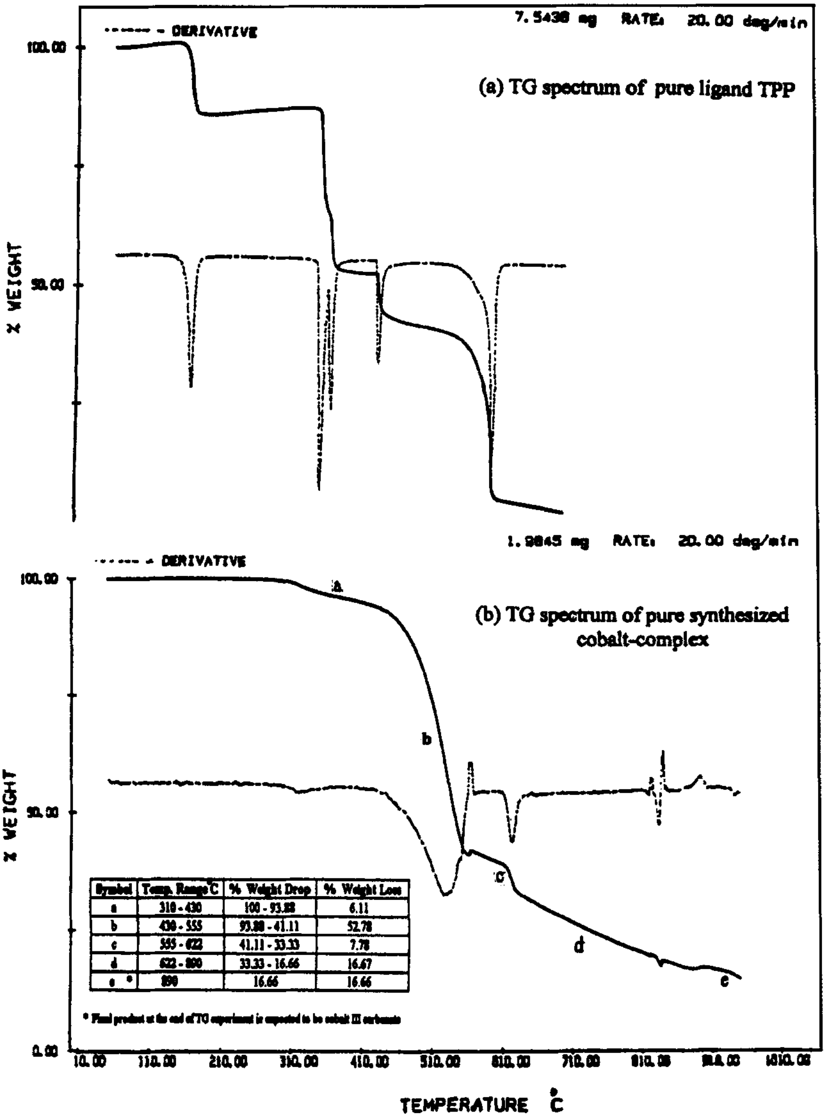
FIGURE 2 Ultra-violet and visible absorption spectra of the ligand TPP and its cobalt-complex in dry Benzene.

TABLE II The elemental analysis data of the synthesized ligand and its corresponding cobalt-complex

Symbol	*Formula*	*Mw*	*Elemental analysis data*		
			C%	*H%*	*N%*
H_2TPP ligand	Found		85.34	4.88	9.14
	Theoretical calculation $C_{44}H_{30}N_4$	614	85.99	4.89	9.12
Cobalt-complex	Found		73.32	4.42	7.65
	Theoretical calculation $C_{45}H_{33}N_4CoOCl$	739.5	73.02	4.46	7.57

agreement with the predicted chemical formula, $C_{45}H_{33}N_4OCoCl$. The calculated molecular weight is 739.5.

Figure 3 shows the thermograms of the pure ligand and its synthesized cobalt complex. A comparison shows the thermal stability of the complex over the ligand. The thermogram of the cobalt complex exhibits four



Symbol	Temp. Range °C	% Weight Drop	% Weight Loss
a	310 - 430	100 - 93.89	6.11
b	430 - 555	93.89 - 41.11	52.78
c	555 - 622	41.11 - 33.33	7.78
d	622 - 890	33.33 - 16.66	16.67
e *	890	16.66	16.66

* Final product at the end of TG experiment is expected to be cobalt III carbonate

FIGURE 3 Thermograms of the pure ligand and its synthesized cobalt-complex.

decomposition stages corresponding to the four practical weight loss percentages calculated as 6.11%, 52.78%, 7.78% and 16.67%, respectively. If one assumes that Co(III) carbonate, is the final stable residual compound, the observed weight loss percentages are consistent. Considering that the weight of the tested sample is taken as 1.9845 mg and assuming the Mw of

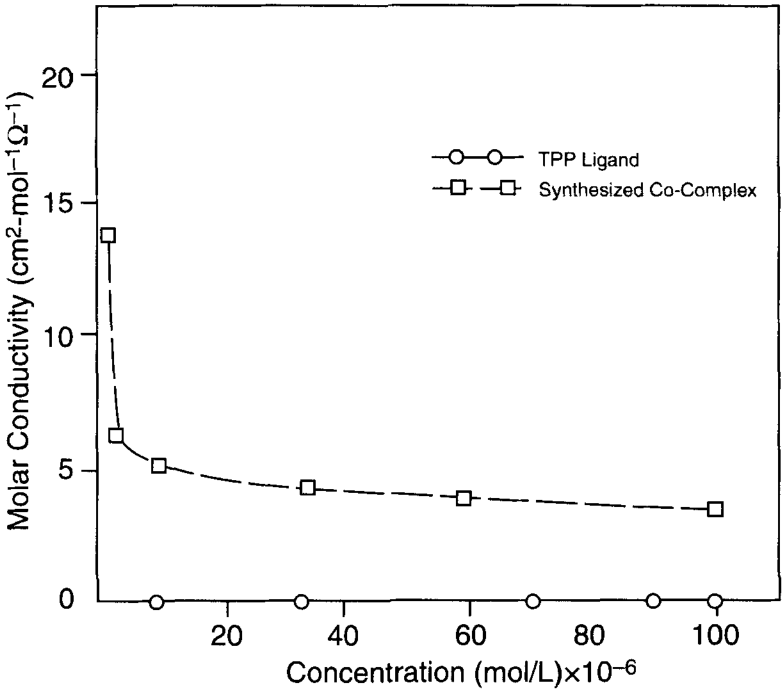


FIGURE 4 Molar conductivity performance of the ligand TPP and its cobalt-complex.

the cobalt complex is 739.5, the calculated number of cobalt ions is 0.85 *i.e.* one cobalt ion is detected for each synthesized complex molecule.

Figure 4 shows the molar conductivity of **H_2TPP** and its cobalt complex. The non-electrolytic conductance of the ligand reveals its non-ionic structure. In contrast, the high conductance of the prepared complex indicates ionic character.

Figure 5 shows the X-ray diffraction patterns of **H_2TPP** and its complex. The comparison indicates that the occurrence of the d-value ($d = 3.06$–3.22 Å), only for the complex, supports the occurrence of the Co–Co bond.

Figure 6 is a comparison between the NMR spectra of the **H_2TPP** and its prepared complex. The comparison indicates alteration in the magnetic environments of the ligand protons, due to metallation. The type, number and assignment for the protons of both the ligand and its complex have been tabulated in Figure 6. It is believed that the peak at far downfield "13.5 ppm" belongs to the proton of HCl. Assuming this is one proton, the number of other protons in the prepared complex is 33.

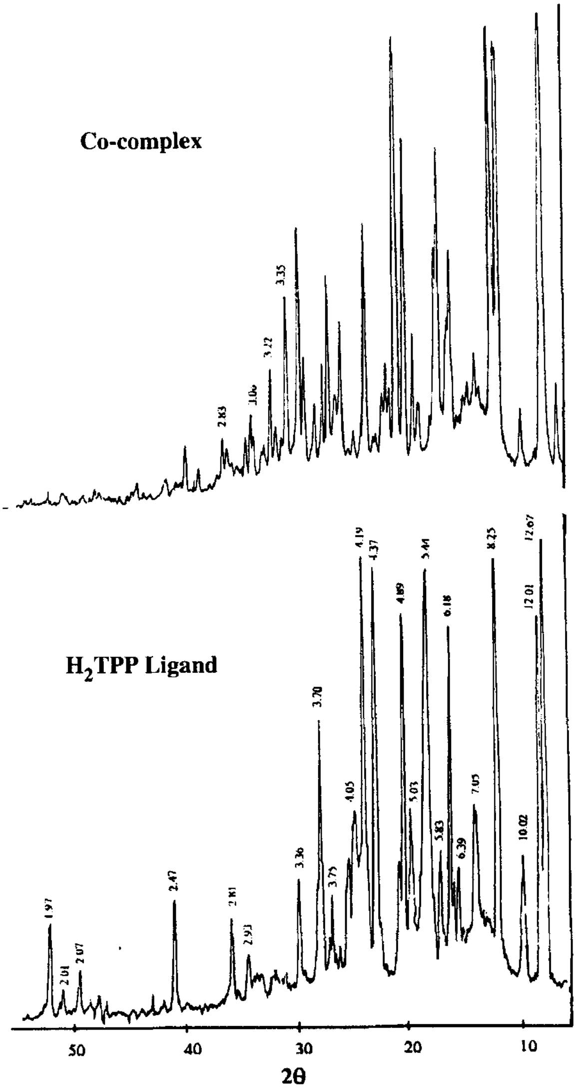
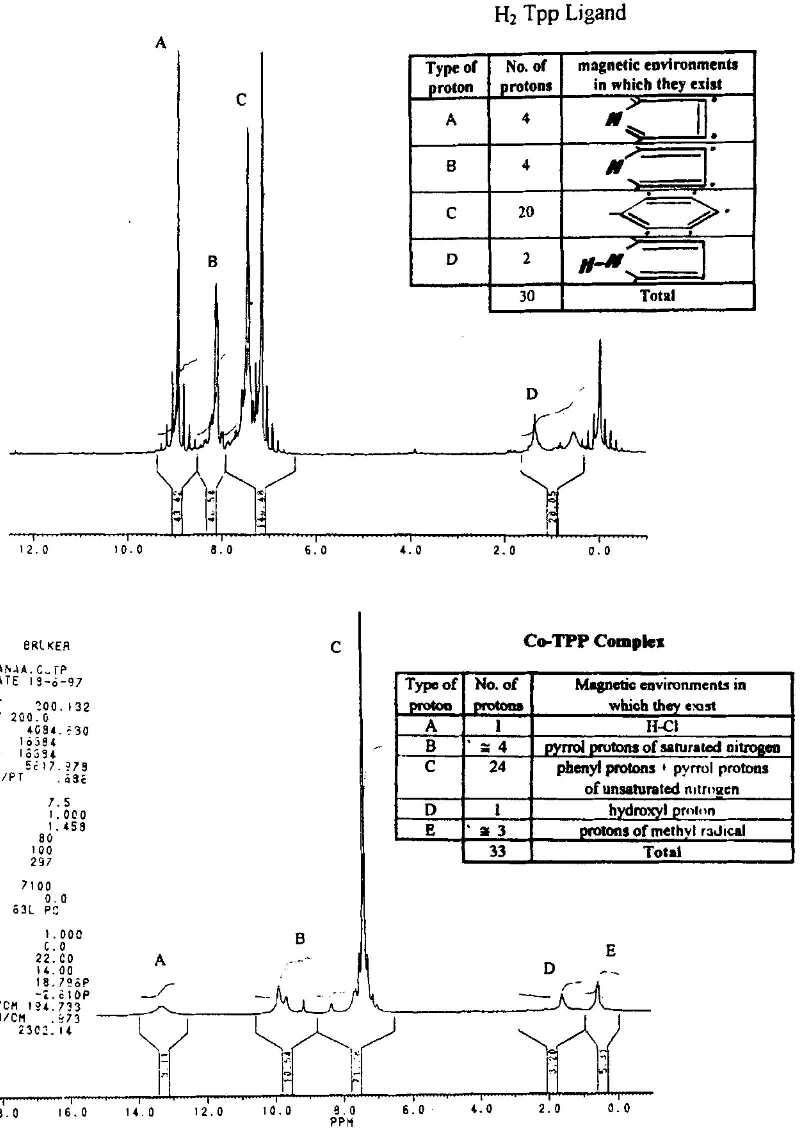


FIGURE 5 X-ray diffraction pattern of H_2TPP and its prepared Co-complex.

Discussion

The metallation of H_2TPP started by forming the dianion TPP^{2-} by removal of the inner pyrrolic-NH protons. The dianion acts as a tetradentate ligand capable of binding a wide varity of divalent metal ions. Consequently, an electrically neutral cobalt complex should form, if Co(II) is introduced as



H2 Tpp Ligand

Type of proton	No. of protons	magnetic environments in which they exist
A	4	
B	4	
C	20	
D	2	
	30	Total

```
BRUKER
HANAA.COTP
DATE 19-6-97

SF     200.132
SY 200.0
O1     4084.630
SI   16384
TD   16384
SW    5617.978
HZ/PT       .686

PW        7.5
RD        1.000
AQ        1.458
RG      80
NS     100
TE     297

FW    7100
O2        0.0
DP   63L PO

LB        1.000
GB        0.0
CX       22.00
CY       14.00
F1       18.796P
F2       -2.610P
HZ/CM 194.733
PPM/CM      .973
SR     2302.14
```

Co-TPP Complex

Type of proton	No. of protons	Magnetic environments in which they exist
A	1	H-Cl
B	≅ 4	pyrrol protons of saturated nitrogen
C	24	phenyl protons + pyrrol protons of unsaturated nitrogen
D	1	hydroxyl proton
E	≅ 3	protons of methyl radical
	33	Total

FIGURE 6 NMR spectra of both ligand and it's cobalt-complex.

$CoCl_2$ to the reaction medium. The result of IR indicate that the cobalt ion is bonded with the four pyrrolic nitrogen atoms by coordination bonds which have been assigned at $\nu 3552\,cm^{-1}$.[27] Moreover, the oxygen atom of CH_3–O–H, also, bonds with the metal ion. Thus, the cobalt ion does not fit in the equatorial plane due to the withdrawal power of oxygen of methyl alcohol; absorption bands at $\nu 1072$, $\nu 1004$, $\nu 835$ and $\nu 794\,\text{cm}^{-1}$ imply no changes in the aromatic skeleton of the TPP^{2-} after complexation.

The presence of axial ligation on the cobalt ion is shown by the following: (i) EDXRF results show chloride in a ratio 1 : 1 with the cobalt ion. To maintain the neutrality of the formed complex, one can consider the H–Cl molecule as a weak ligand bond to the cobalt ion. (ii) Appearance of a stretching band at $1174\,\text{cm}^{-1}$ supports the attachment of oxygen of CH_3–O–H coordinately to a non-carbon atom, probably the cobalt ion. Thus one can deduce that HCl and CH_3OH are axially coordinated with the cobalt ion.

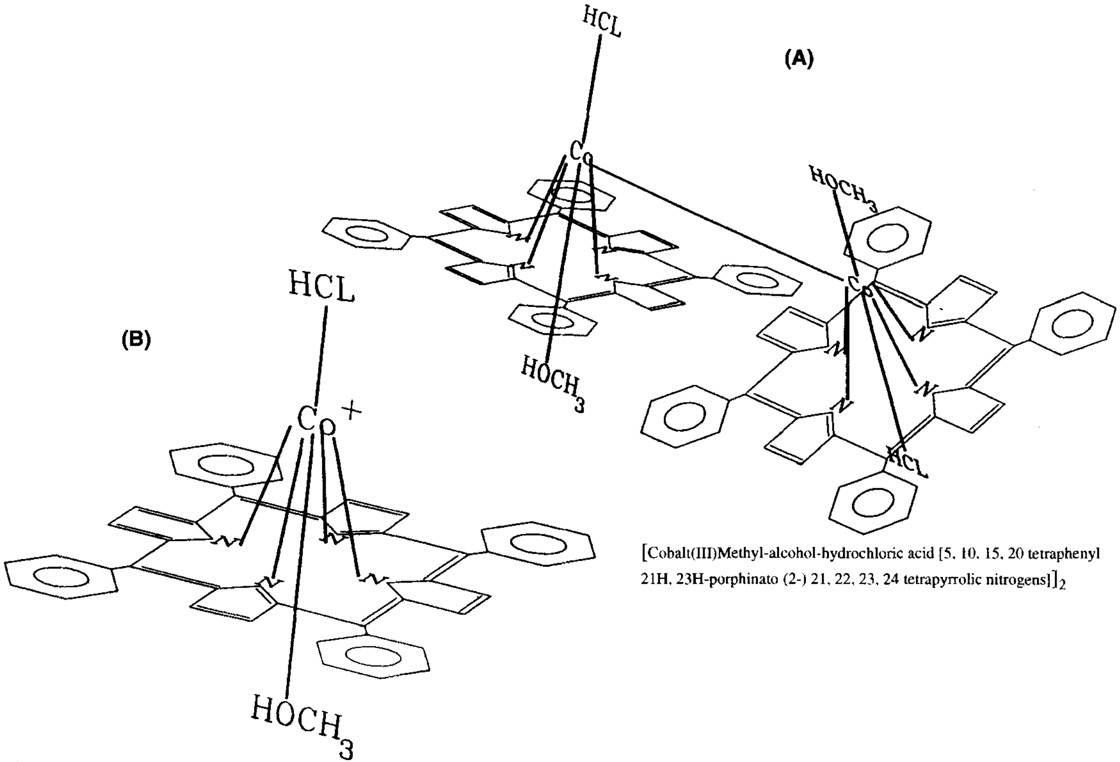
Measurement of magnetic susceptibility indicated the central ion is diamagnetic indicating that the oxidation number is +3 for the cobalt ion. Oxidation to Co^{3+} is facilitated by electron withdrawal of the axial coordinated ligands from the central cobalt ion.

However, decreasing the electron density around the central metal ion, increases the oxidation rate of Co^{2+} to Co^{3+}, especially in the presence of HCl gas dissolved in oxygenated medium at the operating temperature.[4,5] One can attribute the highly conducting phenomenon of the cobalt complex in dry benzene to the residual +ve charge on the cobalt(III) central ion. TGA results ensured that if the final stable compound is a cobaltic salt the ratio 1 : 1 Co^{3+} ion to complex molecule.is computed.

UV–visible spectra of both **H_2TPP** and the cobalt complex showed that metallation of TPP^{2-} leads to a simplification of the visible absorption spectrum to one weak band at 525 nm, while retaining the split Soret absorption at 395 and 411 nm. The weak absorbance band is significantly affected by the nature of the group(s) attatched to the Co^{3+} central ion. For example, if the attached group is only –Cl or –OH anion, the absorbance of the weak band is 502 or 563 nm, respectively.[34]

Direct comparison between the measured and found absorbance values of the one weak band in the visible region indicates that the 525 nm is a combination absorbance for both the $-\overset{..}{\underset{..}{\text{C}}}\text{l}$ and –OH anions which are axially coordinated with the cobalt central ion. Also UV–visible analysis implies no significant change in the conjugation of the TPP^{2-} skeleton, since no long wavelength absorption has been observed. The UV–visible results, showing the axial $\text{H}-\overset{..}{\underset{..}{\text{C}}}\text{l}$ and $H_3C-\overset{..}{\underset{..}{\text{O}}}\text{H}$ compliment the IR results.

Elemental analysis is consistent with the chemical formula $C_{45}H_{33}N_4$-CoOCl for the cobalt complex (see Table II). The calculated number of protons from NMR spectrum of the complex (see Figure 6) is 33. The equality of the total number of protons in both NMR and elemental analysis ensured the precision of the formula.



[Cobalt(III)Methyl-alcohol-hydrochloric acid [5, 10, 15, 20 tetraphenyl 21H, 23H-porphinato (2-) 21, 22, 23, 24 tetrapyrrolic nitrogens]]$_2$

[Cobalt(III)Methyl-alcohol-hydrochloric acid [5, 10, 15, 20 tetraphenyl 21H, 23H-porphinato (2-) 21, 22, 23, 24 tetrapyrrolic nitrogens]]^4

FIGURE 7 A schematic representation of the speculated structures of the prepared Co(III)TPP complex. (A) Co–Co binuclear structure; (B) $[Co(III)TPP]^+$.

The molecular structure of the complex, could be speculated on the basis of energetic instability due to the residual +ve charge on the Co(III) central ion. This remaining +ve charge may cause overlap between cobaltic ions of two complex molecules to form a binuclear Co(III) complex. This is known as M–M back donation. The formation of the Co–Co bond achieves neutrality of the binuclear complex. The length of the Co–Co bond has been predicted from the calculated *d*'s values of the practical XRD pattern of cobalt(III) complex (see Figure 5) in a range of 3.06–3.22 Å.

The longer Co–Co bond than those previously published (2.44–2.59 Å)[36] indicates that while the Co–Co binuclear structure dominates in the solid phase, it is easy to break in solution giving positive ions.

CONCLUSION

On the basis of the results from the different spectroscopic and physicochemical analyses, the cobalt complex has two stable molecular structures:

(a) In the solid phase, the Co–Co binuclear molecule dominates to achieve neutrality (see Figure 7A).
(b) If the Co(III)-complex is dissolved in a solution, the charged structure is formed due to breaking of the Co–Co bond (see Figure 7B).

These structures might provide suprabiotic catalysts for the following reasons:

(a) Electron withdrawal from the metal center by axially coordinated ligands results in a high Co(III)/Co(II) ratio.
(b) Large steric constraints plus the geometry of the Co–Co binuclear molecule, increase the immobilization properties, when it is loaded on conventional or non-conventional supports. This will lead to an increase in the commercial importance of oxidation catalysts.

Valuable catalyst(s) might be prepared by introducing minor modifications.

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