Cobalt(II) Derivatives of Cyclic Phosphazenes: Synthesis, Characterization and Fungicidal Behaviour

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Cobalt(II) Derivatives, Cyclic Phosphazenes, IR Spectra

Chlorine atoms of hexachlorocyclotriphosphazene were substituted with $-NH.C_2H_5$, $-NH.CH_2C_6H_5$ and $-OC_2H_5$ to yield organotriphosphazene ligands. Anhydrous cobalt(II) chloride formed a number of addition complexes with these ligands in different stoichiometric ratios. On the basis of electronic and IR spectra, magnetic moment, conductivity measurements and molecular weight determination, structures of these complexes have been suggested. The complexes were screened for their antifungal activities against *Aspergillus flavus* and *Aspergillus niger*.

Introduction

Rapid advances in covalent inorganic polymer research and technology are taking place in the field of cyclic phosphazene polymers [1,2]. The cyclic phosphazenes constitute one of the largest and most widely studied groups of heterocycles based on inorganic skeleton with regard to π -bonding, delocalisation and aromaticity in the rings [3-5]. Extensive studies have been carried out on cyclophosphazenes keeping in view the potential applications of these derivatives as ultrahigh-capacity fertilizers [6], pesticides [7] and insecticides [8]. Due to the presence of electron lone pair on each nitrogen atom of the skeleton, phosphazenes can easily bind a proton or complex with electron deficient molecules. Compared to the addition compounds of cyclophosphazenes with electron deficient compounds of non-transition elements (e.g. Al [9], Si [10], As [11] and Sb [12] etc.), the derivatives with transition elements have received little attention [2]. Witt et al. have reported the synthesis and structural elucidation of some transition metal derivatives of open and cyclo-phosphazenes [13-19]. They took early transition elements to synthesize these derivatives in which the transition metal occupies the position in the ring of the cyclophosphazenes.

In the present paper we report the synthesis of some cyclophosphazene complexes of cobalt(II),

one of the later transition elements, in which cobalt(II) is lying outside the ring. The complexes have been characterized by their elemental analyses, infra red and electronic reflectance spectra, magnetic moment and molecular weight determinations, and conductivity behaviour. Their fungicidal activity has also been studied.

Experimental

Materials

Anhydrous $CoCl_2$ was prepared by heating its hexahydrate (BDH) in a current of dry HCl gas and analysed.

Calcd	Co 45.39	Cl 54.61%,
Found	Co 45.32	Cl 54.20%.

Ethylamine (BDH) was used as such. Benzylamine was distilled (b.p. 185 °C) before use. PCl_5 and NH_4Cl used were of analytical grade. PhH and EtOH were dried by the standard literature procedures [20].

Analytical and physical methods

Cobalt was estimated as cobalt anthranilate [21], chloride as AgCl and nitrogen by the standard Kjeldahl method.

IR spectra were recorded on a Perkin-Elmer (model 557) spectrophotometer, electronic spectra on a Hitachi model U-2000 spectrophotometer.

Electrical conductances were measured on a Beckman RC-18A conductivity bridge. Magnetic susceptibility measurements were carried out on a Gouy balance using analytical grade ferrous am-

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monium sulphate as standard. Molecular weights of the complexes were determined cryoscopically in benzene.

Synthesis of phosphazene ligands

Phosphorus pentachloride (10.40 g) and ammonium chloride (2.16 g) were refluxed in PhMe (100 cm³) for 4 h. From the reaction mixture hexachlorocyclophosphazene was crystallized out in carbon tetrachloride (75 cm³) as a colourless solid (m.p. 115 °C). The chlorine atoms of this cyclic trimer (NPCl₂)₃ were substituted by -NH.Et, -NH.CH₂ Ph and -OEt by treating it with EtNH₂, PhCH₂NH₂ or NaOEt respectively in 1:6 molar ratio using PhMe as solvent under reflux (3 h). The synthesized ligands can be represented as follows:



Synthesis of the complexes

Cyclophosphazene ligand, L^1 , (4.54 g) was added to anhydrous cobalt(II) chloride (1.47 g)

dissolved in EtOH (40 cm³). Refluxing (1 h) and removal of excess solvent *in vacuo* (50 °C/1 mm) yielded blue sticky solid. This solid was dissolved in EtOH (15 cm³) and reprecipitated with carbon tetrachloride (60 cm³) and finally dried *in vacuo*.

Precautions were taken to exclude moisture throughout. The same procedure was adopted to synthesize other complexes and the details are given in Table I. Characteristic data and molecular weights of some complexes are also listed in Table I.

Results and Discussion

Cyclophosphazene ligands are prepared by the following reactions:

$$nPCl_5 + nNH_4Cl \xrightarrow{Ph Me} (NPCl_2)_n + 4nHCl \uparrow$$
 (1)

(where n = 3,4 or 5) The cyclic trimer is crystallised in CCl₄.

$$\underbrace{ \begin{bmatrix} Cl & Cl \\ N = P \end{bmatrix}_{3}^{} + 6 \text{ R.NH}_{2} \underbrace{ \frac{Ph Me}{reflux}}_{\text{reflux}} \underbrace{ \begin{bmatrix} R.NH & NH.R. \\ N = P \end{bmatrix}_{3}^{} + 6HCl \uparrow (2)$$
(Where R = -Et or -CH, Ph)

$$\frac{\text{Cl Cl}}{\left[N = P \right]_{3}^{3} + 6 \text{ NaOEt}} \xrightarrow{\text{Ph H}}_{\text{reflux}} \frac{\text{OEt OEt}}{\left[N = P \right]_{3}^{3}} + 6 \text{NaCl} \downarrow (3)$$

Table I	. 1	Reaction	products	of	cob	alt($(\Pi$) c	hlori	de	wit	th p	hosp	hazene	ligand	
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Reactan (g)	its*		Molar ratio	Product and colour	F Co (%)	Found (Calcd) Cl (%)) N (%)	Mol. Wt.
Co Cl ₂ (1.47)	+	L ¹ (4.54)	1:1	L ¹ (Co Cl ₂ . EtOH) Blue sticky solid	10.13 (10.24)	12.20 (12.32)	21.17 (21.90)	561 (575)
Co Cl ₂ (3.78)	+	L^1 (5.81)	2:1	L^1 (Co Cl ₂ . EtOH) ₂ Blue solid	15.48 (15.69)	18.69 (18.87)	16.46 (16.78)	772 (751)
Co Cl ₂ (5.61)	+	L ¹ (5.78)	3:1	L^1 (Co Cl ₂ . EtOH) ₃ Blue solid	19.12 (19.06)	23.01 (22.94)	13.35 (13.60)	906 (927)
Co Cl ₂ (0.82)	+	L ² (4.88)	1:1	L ² (Co Cl ₂ . EtOH) Light Blue solid	6.15 (6.22)	7.42 (7.48)	12.93 (13.30)	_
Co Cl ₂ (2.02)	+	L ² (6.04)	2:1	L^2 (Co Cl ₂ . EtOH) ₂ Blue solid	10.31 (10.49)	12.74 (12.62)	11.08 (11.22)	-
Co Cl ₂ (2.32)	+	L^{2} (4.60)	3:1	L^2 (Co Cl ₂ . EtOH) ₃ Blue solid	13.46 (13.60)	16.16 (16.37)	9.81 (9.70)	-
Co Cl ₂ (1.56)	+	L ³ (4.88)	1:1	L ³ (Co Cl ₂ . EtOH) Blue solid	9.97 (10.14)	11.96 (12.20)	7.09 (7.23)	574 (581)
Co Cl ₂ (2.27)	+	L^{3} (3.56)	2:1	L^3 (Co Cl ₂ . EtOH) ₂ Blue solid	15.34 (15.57)	18.41 (18.73)	5.31 (5.55)	-
Co Cl ₂ (3.06)	+	L ³ (3.21)	3:1	L ³ (Co Cl ₂ . EtOH) ₃ Dark blue solid	18.63 (18.95)	22.68 (22.80)	4.63 (4.50)	_

* In refluxing ethanol (EtOH).

Addition complexes of cobalt(II) chloride with above phosphazene ligands were synthesized using EtOH solvent in different molar ratios:

$$x \operatorname{CoCl}_2 + L \xrightarrow{\text{EtOH}} L. (\operatorname{CoCl}_2.)_x$$

(Where L is cyclophosphazene ligand and x=1,2 or 3).

The reactions are facile and the products are obtained in quantitative yield as blue solids. The molar conductance measurements in their benzene solution show that all the complexes behave as non-electrolytes (λ m values obtained were less than 0.6 ohm⁻¹ cm² mol⁻¹).

The appearance of a band in their i.r. spectra at \sim 3160 cm⁻¹ is due to v(OH) stretching of EtOH coordinated to cobalt. It is much lower than 3300 cm⁻¹ at which the same band appears in free alcohol. The new band observed below 700 cm⁻¹ is due to coordination of phosphazene ring nitrogen to cobalt.

In the electronic spectra of the above complexes in the region $11000-25000 \text{ cm}^{-1}$ a single band is observed at $15000\pm200 \text{ cm}^{-1}$. This is assigned as v_3 band of cobalt(II) [${}^{4}A_{2} \rightarrow {}^{4}T_{1}$ (P)] in a tetrahedral environment [22]. This band is quite comparable to the band obtained for [CoCl₄]²⁻ in which Co²⁺ is in tetrahedral environment [23]. The blue colour of the above cobalt(II) complexes also supports the above view. This is in contrast to the octahedral environment around cobalt(II) in CoCl₂ and [Co(H₂O)₆]²⁺ [22] where two electronic bands are found in $11000-25000 \text{ cm}^{-1}$.

The magnetic moments of the complexes were found in the range of 4.6–4.7 B.M. These values are in accordance with the tetrahedral geometry around cobalt(II) in the above complexes [23].

Molecular weights of some of the above complexes were determined cryoscopically in benzene. The values reported in Table I suggest that the complexes are monomeric.

Four complexes were screened for their antifungal activity against *Aspergillus flavus* and *Aspergillus niger* at 1000, 100 and 10 ppm concentrations. The results have been compared with the standard fungicide Dithane M-45, tested under similar conditions. The percentage inhibition was calculated by using the formula:

% inhibition = $(C-T)/C \times 100$

Where, C=Diameter of fungus colony (in mm) in controlled plate and T=Diameter of fungus (in mm) in treated plate.

The data given in Table II show the effect of fungicidal behaviour due to different substituents on the polyphosphazene ligands. It is clear that the hexaethoxy triphosphazene complexes have the maximum inhibition against both the fungi. *A. flavus* and *A. niger*. On the otherhand hexabenzyl-aminotriphosphozene complex has the least reactivity against these fungi. The data further suggest that the fungicidal activities of all the synthesized complexes are not comparable with commercial fungicide Diathane M-45.

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Table II	. Fungicidal	activity	of the	comp.	lexes.
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Complex	Р	ercentage	inhibition	after	96 1	h	against
		A. flav	vus at		A. nige	r at	
	1000 ppm	100 ppm	10 ppm	1000 ppm	100 ppm	10 ppm	
$ \begin{array}{c} L^1 \ (\text{Co } \text{Cl}_2. \ \text{EtOH}) \\ L^1 \ (\text{Co } \text{Cl}_2. \ \text{EtOH})_3 \\ L^2 \ (\text{Co } \text{Cl}_2. \ \text{EtOH})_2 \\ L^3 \ (\text{Co } \text{Cl}_2. \ \text{EtOH})_2 \\ \text{Dithane } M-45 \end{array} $	54 59 47 65 93	42 48 39 54 89	29 40 34 48 82	52 54 48 63 90	44 46 42 55 80	36 39 36 49 77	

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