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Enviro-economic Synthesis, Characterization and Antibacterial Study of O-Alkyl or O-Aryl Trithiophosphates of Cadmium

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Abstract Cadmium (II) O-alkyl or O-aryl trithiophosphate of the type $Cd[KS(S_2)POR]_2$ (where R= Me, Et, Pr^i, Bu^i, Ph, CH_2Ph) have been synthesized by an environmentally harmless, efficient and quick smooth way from the reaction of cadmium chloride and dipotassium salt of O-alkyl or O-aryl trithiophosphates in 1:2 molar ratio. They are synthesized by solvent free conditions and microwave assisted procedure. These derivatives are yellow colour solids, insoluble in common organic solvents but are soluble in DMSO, DMF and pyridine. These have been characterized by elemental analysis, molecular weight determinations and spectroscopic(IR, ^1H and ^{31}P NMR) studies. On the basis of them square planar geometry has been proposed for these derivatives. The newly synthesized complexes show effectiveness against gram positive and gram negative bacteria and a comparative study of antibacterial effect of synthesized compounds with standard drugs has also been investigated.

Keywords: *cadmium chloride, dipotassium salts of O-alkyl or O-aryl trithiophosphates, solvent free conditions, microwave assisted procedure, antibacterial activity*

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1. Introduction

In recent years, the outcome of investigation on metal, organometal and organic derivatives of phosphate and dithiophosphate (open chain and cyclic) ester [1,2,3,4] was interested to extend the investigation on trithiophosphate ligand [5,6]. The chemists are taking interest for the synthesis of co-ordination compounds with sulphur containing ligands [7,8,9,10,11,12].

The survey of literature reveals that the dialkyl dithiophosphate derivatives of cadmium has also been considerable interest because of their crystallographic studies [13,14], structural features and industrial applications as oil additives [15]. Potassium salt of O-alkyl trithiophosphates show two isomeric form $[(RO)P(S)S_2]$ (thiono) and $[(RS)P(O)S_2]$ (thiolo) [16] which have interesting chemical bonding modes in metal and organometal derivatives [17,18].

Cadmium compounds are poisonous but it has certain commercial and medical uses. Cadmium compounds are used as protection from corrosion in the production of batteries and accumulators. Cadmium is used in many kinds of solder and bearing alloys, because it has a low coefficient of friction and fatigue resistance. It is also used as pigment in dye, glass, ceramics, and enamel manufacture. Cadmium compounds are used commercially in metallurgy, photography and electrochemistry. Some of the cadmium compounds have been used as ascaricides, antiseptics and fungicides. Some metal derivatives of thiophosphate ligands [17,19,20,21,22] have received considerable attention for synthesizing and screening antibacterial activity.

Microwave irradiation is used for chemical reactions [23,24,25,26] to synthesize newly trithiophosphate derivatives of cadmium. Microwave assisted method is beneficial than conventional methods because it requires lower energy, increases rate of reaction, gives higher yield and required milder reaction conditions. Although O-alkyl/O-aryl trithiophosphate of transition metals [27,28,29] have been studied in our laboratories. The cadmium derivatives of trithiophosphate ligand have not been synthesized and does not study their antibacterial effect as yet.

In view of this it was considered worthwhile to synthesize and characterize O-alkyl or O-aryl trithiophosphate derivatives of cadmium, study their antibacterial effect and compare their antibacterial activities with standard drugs.

2. Experimental

Methods were reported in the literature [30] for synthesizing dipotassium salts of O-alkyl or O-aryl

trithiophosphates. All the solvents were of analytical grade during present investigation. Carbon and hydrogen were estimated by Coleman C, H and N analyzer. Sulphur has estimated by Messenger's method [31] and cadmium was estimated by gravemetric method. Molecular weights were determined by Knauer Vapour pressure osmometer in chloroform. FTIR spectra were recorded on a Perkin Elmer 10.400 spectrophotometer in the range of 4000-200cm^{-1}. ^{1}H NMR spectra were recorded in $CDCl_3$ and ^{31}P NMR spectra were recorded in DMSO-d_6 on DELTA 2 NMR 300 MHz spectrophotometer using TMS(for ^{1}H) and H_3PO_4(for ^{31}P) as an external reference.

3. Synthesis of $Cd[K(S)(S_2)POCH_3]_2$

Cadmium chloride 0.8528g [4.2358mmol] and dipotassium salt of O-methyl trithiophosphate 2.0008g [8.4725mmol] in (1:2) molar ratio were taken in R.B.F. This mixture was put into microwave for 2 minutes. Then the reaction mixture was dissolved by minimum amount of distilled water, after filteration the white to yellow coloured solid was obtained. It was washed 2-3 times with ethanol and dried to yield a yellow powdery solid (4.0520g) in 94% yield [Table 1].

Analysis %calcd.for $Cd[K(S)(S_2)POCH_3]_2$

C=4.73; H=1.19; S=37.94; Cd=22.17

Found C=4.63;H=1.08; S=36.82; Cd=21.92

Rest of the derivatives were synthesized by similar method.

4. Results and Discussion

Dipotassium salt of O-alkyl or O-aryl trithiophosphates react with cadmium chloride in 1:2 molar ratio by using solvent free microwave assisted method for higher yield.

$CdCl_2 + ROP(S)(SK)_2 \longrightarrow Cd[K(S)(S_2)POR]_2 + 2KCl$ (where R=Me, Et, Pr^{i}, Bu^{i}, Ph, CH_2Ph)

Above reaction was completed in microwave within 2 minutes. Then the reaction mixture was dissolved in minimum amount of distilled water, after filteration the obtained precipitate were separated as white to yellow coloured solid. Adding 20mL ethanol in it, yellow powdery solid was obtained. Potassium chloride was removed in filterate. These products were washed two-three times with ethanol and recrystallized. The products were separated yellow coloured powdery solids. These complexes were insoluble in common organic solvents but soluble in coordinated solvents like DMSO, DMF, etc. In methanol these complexes are sparingly soluble.

Conventional method was also used for the synthesis of these derivatives. Cadmium chloride was taken with dipotassium salt of O-alkyl or O-aryl trithiophosphate in 1:2 molar ratio in distilled water, respectively. The reaction mixture was refluxed for 3-4 hrs. Potassium chloride was removed in filterate. The yellow coloured precipitate was formed. The obtained yellow colour solid were washed and recrystallized.

It was concluded that the yield of product in microwave assisted method is more than conventional method.

Table 1. Synthetic and Analytical Data of $Cd[K(S)(S_2)POR]_2$

S.NO	Reactant …. g …. (mmol)		Molar Ratio	Product ..…. g …... %	Analysis % Found (Calcd.)				Molecular Weight Found (Calcd.)
	$CdCl_2$	**$ROP(S)(SK)_2$ R... or Ar…**			**C**	**H**	**S**	**Cd**	
1	0.8528 [4.2358]	CH_3 2.0008 [8.4725]	1:2	$Cd[K(S)(S_2)POCH_3]_2$ 4.0520 94	4.63 (4.73)	1.08 (1.19)	36.82 (37.94)	21.92 (22.17)	503.14 (506.96)
2	0.8366 [4.1553]	C_2H_5 2.0780 [8.3106]	1:2	$Cd[K(S)(S_2)POC_2H_5]_2$ 4.0905 92	7.89 (8.97)	1.15 (1.88)	34.32 (35.95)	20.34 (21.01)	-
3	0.7640 [3.7947]	$^{i}C_3H_7$ 2.0048 [7.5896]	1:2	$Cd[K(S)(S_2)PO^{i}C_3H_7]_2$ 4.0597 95	12.01 (12.79)	2.15 (2.50)	33.75 (34.16)	19.12 (19.96)	-
4	0.7269 [3.6109]	$^{i}C_4H_9$ 2.0087 [7.2216]	1:2	$Cd[K(S)(S_2)PO^{i}C_4H_9]_2$ 3.9698 93	15.95 (16.25)	2.77 (3.06)	31.98 (32.54)	18.54 (19.01)	-
5	0.6758 [3.3567]	C_6H_5 2.0018 [6.7140]	1:2	$Cd[K(S)(S_2)POC_6H_5]_2$ 3.9828 94	22..07 (22.83)	1.22 (1.59)	29.96 (30.48)	17.08 (17.81)	-
6	0.6528 [3.2424]	o-CH_3-C_6H_4 2.0245 [6.4856]	1:2	$Cd[K(S)(S_2)POC_6H_4CH_3]_2$ 3.9329 92	24.75 (25.50)	1.79 (2.14)	28.86 (29.18)	16.50 (17.05)	657.2 (659.14)
7	0.6456 [3.2067]	m-CH_3-C_6H_4 2.0022 [6.4142]	1:2	$Cd[K(S)(S_2)POC_6H_4CH_3]_2$ 4.0164 95	24.75 (25.50)	1.79 (2.14)	28.86 (29.18)	16.50 (17.05)	-
8	0.6530 [3.2434]	p-CH_3-C_6H_4 2.0249 [6.4869]	1:2	$Cd[K(S)(S_2)POC_6H_4$-$CH_3]_2$ 3.9764 93	24.75 (25.50)	1.79 (2.14)	28.86 (29.18)	16.50 (17.05)	-

Table 2. IR Spectral Data of $Cd[K(S)(S_2)POR]_2$

S.No.	COMPOUND	ν(P)-O-C	νP-O-(C)	νP=S	νP-S	νCd-S
1	$Cd[K(S)(S_2)POCH_3]_2$	1258.6s	1076.7s	682.5s	580.2s	509.8m
2	$Cd[K(S)(S_2)POC_2H_5]_2$	1241.9s	995.4m	698.2s	589.6m	438.4w
3	$Cd[K(S)(S_2)PO^iC_3H_7]_2$	1100.3s	960.1vs	635.4m	533.1s	452.4s
4	$Cd[K(S)(S_2)PO^iC_4H_9]_2$	1164.7s	994.4vs	630.2s	658.7vs	554.4s
5	$Cd[K(S)(S_2)POC_6H_5]_2$	1191.9s	1075.8m	613.8m	584.3m	482.7w
6	$Cd[K(S)(S_2)POC_6H_4$-$CH_3]_2$ o-	1198.2s	935.5s	649.4s	579.2s	478.6m
7	$Cd[K(S)(S_2)POC_6H_4$-$CH_3]_2$ m-	1195.7s	924.7s	658.6s	564.4m	474.5s
8	$Cd[K(S)(S_2)POC_6H_4$-$CH_3]_2$ p-	1192.4vs	900.1vs	672.5vs	552.8m	472.6m

Vs = very strong, s = strong, m = medium, w = weak.

5. IR Spectra

The IR spectra of these complexes have been recorded in the range of 4000-200cm^{-1} (Table 2) and following characteristics were observed:-

(i) The bands present in the region 1258.6- 1100.3 cm^{-1} and 1076.7- 924.7 cm^{-1} have been assigned to **ν**(P)-O-C and **ν**P-O-(C) stretching modes, respectively [32].

(ii) A strong intensity band present in the region 698.2- 613.8 cm^{-1} and 658.7- 533.1 cm^{-1} has been attributed to νP=S and νP-S frequencies, respectively. Shifting of bands towards lower wave number (12-40 cm^{-1}) from parent trithiophosphate indicates attachment of P=S and P-S group through sulphur atom to cadmium in these derivatives.

(iii) The absorption band in the region 554.4-438.4 cm^{-1} has been assigned the formation of cadmium sulphur bond [33].

6. NMR Spectra

^{1}H NMR Spectra

The PMR spectra were recorded in 300.13 MHz region. The synthesized compounds are insoluble in other solvents so PMR spectra could be determined in DMSO-d_6. Due to alkoxy and phenyl protons, these derivatives show characteristics resonance signals. In trithiophosphate derivatives of cadmium the signal shift to higher field in the region 1.32 ppm due to methyl protons. The characteristic resonance signals due to OCH_3, OCH_2, OCH, OC_6H_5, $OCH_2C_6H_5$ protons are present in the expected region [17,20].

^{31}PNMR Spectra

A single resonance signal for these derivatives were obtained in the region 104.7- 116.1 ppm. Signals were shifted to downfield (δ 20- 30 ppm) as compared to parent trithiophosphate (Table 3) shows bidentate mode of bonding of ligand moiety in newly synthesized compounds.

7. Antibacterial Activity

The newly synthesized complexes were screened for their antibacterial activity against gram-positive and gram-negative bacteria (Table 4). This activity was done by the paper disc method and DMF was used as a solvent. The zone of inhibition was measured in mm. The newly synthesized complexes were tested at 100µg/mL concentration. The observations show that compounds 10, 11, 12, 13 are more effective against gram positive bacteria and compounds 14, 15, 16, 17 are more effective against gram negative bacteria.

Table 3. ^{1}H NMR and ^{31}P NMR Spectral Data of $Cd[K(S)(S_2)POR]_2$

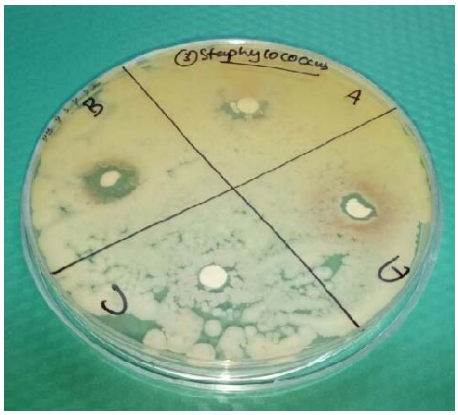
S.No.	COMPOUND	^{1}H Chemical Shift (δ-----PPm)	^{31}P Chemical Shift (δ-----PPm)
1	$Cd[K(S)(S_2)POCH_3]_2$	3.25, s, 6H(OCH_3)	116.10
2	$Cd[K(S)(S_2)POC_2H_5]_2$	1.62, t, 6H(CH_3) 3.48, q, 4H(OCH_2)	114.30
3	$Cd[K(S)(S_2)PO^iC_3H_7]_2$	1.25, d, 12H(CH_3) 3.44-3.39, m, 2H(OCH)	107.40
4	$Cd[K(S)(S_2)PO^iC_4H_9]_2$	1.45, d, 12H(CH_3) 2.61-2.35, m, 2H(CH) 3.22, d, 4H(OCH_2)	104.70
5	$Cd[K(S)(S_2)POC_6H_5]_2$	6.69-6.46, m, 10H(OC_6H_5)	114.50
6	$Cd[K(S)(S_2)POC_6H_4$-$CH_3]_2$ o-	3.8, s, 6H(CH_3) 6.98-6.75, m, 8H(OC_6H_4)	112.40
7	$Cd[K(S)(S_2)POC_6H_4$-$CH_3]_2$ m-	3.43, s, 6H(CH_3) 7.35-7.11, m, 8H(OC_6H_4)	109.70
8	$Cd[K(S)(S_2)POC_6H_4$-$CH_3]_2$ p-	3.5, s, 6H(CH_3) 7.25-7.00, m, 8H(OC_6H_4)	107.50

s= singlet, d = doublet, t = triplet, q = quartet, m = multiplet

Table 4. Antibacterial activity of Cadmium derivatives of the type $Cd[K(S)(S_2)POR]_2$

Sr. No.	Compund	Gram positive bacteria zone of inhibition in mm	Gram negative bacteria zone of inhibition in mm
1.	Solvent	0	0
2.	$CH_3OPS(S)(SK)_2$	9	6
3.	$C_2H_5OPS(S)(SK)_2$	7	5
4.	$^{i}PrOP(S)(SK)_2$	10	4
5.	$^{i}BuOP(S)(SK)_2$	6	8
6.	$PhOP(S)(SK)_2$	10	12
7.	o-CH_3 $PhOP(S)(SK)_2$	12	14
8.	m-CH_3 $PhOP(S)(SK)_2$	11	13
9.	p-CH_3 $PhOP(S)(SK)_2$	9	10
10.	$Cd[K(S)(S_2)POCH_3]_2$	22	11
11.	$Cd[K(S)(S_2)POC_2H_5]_2$	28	15
12.	$Cd[K(S)(S_2)PO^{i}C_3H_7]_2$	32	14
13.	$Cd[K(S)(S_2)PO^{i}C_4H_9]_2$	26	19
14.	$Cd[K(S)(S_2)POC_6H_5]_2$	16	20
15.	$Cd[K(S)(S_2)POC_6H_4\text{-}CH_3]_2$ o-	13	22
16.	$Cd[K(S)(S_2)POC_6H_4\text{-}CH_3]_2$ m-	18	26
17.	$Cd[K(S)(S_2)POC_6H_4\text{-}CH_3]_2$ p-	10	24
18.	Imipenem	12	30
19.	Linezolid	8	10

Effect of $Cd[K(S)(S_2)PO^{i}C_3H_7]_2$ on gram positive and gram negative bacteria



Effect on gram positive bacteria

Effect on gram negative bacteria

A. Solvent, B. Ligand, C. $CdCl_2$, D. $Cd[K(S)(S_2)PO^{i}C_3H_7]_2$

Effect of $Cd[K(S)(S_2)POC_6H_4\text{-}CH_3]_2$ on gram positive and gram negative bacteria

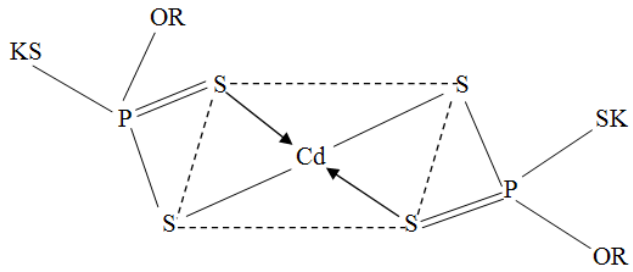
Effect on gram positive bacteria

Effect on gram negative bacteria

1. Solvent, 2. Ligand, 3. $CdCl_2$, 4. $Cd[K(S)(S_2)POC_6H_4\text{-}CH_3]_2$

8. Conclusion

The authentic structure of newly synthesized complexes by us could not be determined by X-ray crystallography due to non –availability of suitable crystals, however on the basis of physico-chemical (elemental analysis, molecular weight determination) and spectroscopic data (IR, ^{1}H, ^{31}P), the structure of complexes may be as follows:-



On the basis of spectroscopic studies, a square planar geometry for these complexes has been suggested.

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