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Research Article

SYNTHESIS AND CHARACTERIZATION OF O-ALKYL OR O-ARYL TRITHIOPHOSPHATE DERIVATIVES OF CHROMIUM (III)

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ABSTRACT

Complex of the type $Cr[R\text{-}O\text{-}P(S)S_2]_3$ where (R= Me, Et, Pr^i, Bu^i, ph.) have been synthesized by the reactions of chromium trioxde (CrO_3) and O-alkyl / O-aryl trithiophosphoric acid in 1:3 molar ratio in anhydrous benzene. O-alkyl / O-aryl trithiophosphate derivatives of chromium are light brown coloured monomeric solid which are soluble in common organic solvents. These complex have been characterized by elemental analysis, (C,H,S) molecular weight measurement, IR and NMR (^1H, ^{12}C, ^{31}P) spectral studies. On the basis of above studies octahedral geometry of O-alkyl/O-aryl trithiophosphate derivatives of chromium has been suggested, which are consists with six coordinated chromium and bidentate behaviour of the trithiophosphate moiety.

INTRODUCTION

The development of organometallic chemistry during the last two decades indicates that synthesis and applications of organometallics in organic synthesis continue to be pursued actively and represents a fruitfull area of research[1-6]. O-alkyl/ O-aryl trithiophosphato derivatives find extensive applications in various fields, like agriculture[7-9], industries[10-11], analytical studies[12-13]. O-alkyl/O-aryl trithiophosphates $[R\text{-}OP(S)(SH)_2]$ are important phosphorus-sulphur containing ligands which provide various bonding aspects with metal and metalloids[14-17]. O-alkyl trithiophosphate ester have been used as defoliants[18], insecticides[19], nematodicides[20] and inhibitor of steel corrosion[21]. Although some metal complexes of O-alkyl trithiophosphates have also been reported in the literature. Yet the chemistry of O-alkyl/O-aryl trithiophosphates of chromium not explored. Hence it is worthwhile to synthesize chromium (III) derivatives of O-alkyl/O-aryl trithiophosphates to study their interesting bonding modes[22-25].

Experimental

O-alkyl and O-aryl trithiophosphoric acid are prepared by a method reported earlier [26]. The estimation of carbon and hydrogen are done by a Coleman C, H, N, analyzer. Messenger's method is used for sulphur estimation[27] and chromium was determined by the literature method[27]. FTIR spectra were recorded on Perkin Elmer spectrum version 10.4.00 spectrophotometer in the range 4000-200cm^{-1}. ^1H NMR spectra were recorded in dutereted DMSO and ^{31}P NMR spectra were recorded in DMSO-D_6 on DELTA 2- NMR 400 MHz spectrophotometer using TMS (for ^1H) as external reference.

Synthesis of $Cr[CH_3OP(S)S_2]_3$

In a dried 100 mL R.B.F O-methyl trithiophosphoric acid 2.0000 g [12. 4879mmol] and chromium trioxide 0.4162g [4.1624mmol] in1:3 molar ratio are taken 30 mL benzene. Condensor is fitted on R.B.F. The content is reflexed on the heating mentle for 8- 10 hrs. A clear solution is obtained initially then brown powdery solid appeared. Water formed during the course of reaction removed azeotropically with benzene. After filtration brown powdery solid is washed three-four times with acetone and n-hexane then dried. Analysis calcd. for $Cr[S_2P(S)OCH_3]_3$ C=6.83; H=1.70; S=54.80; Found C=6.63; H=1.61; S=53.20; Rest derivatives are synthesized by similar method.

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RESULTS AND DISCUSSION

Reactions of chromium trioxide with O-alkyl or O-aryl trithiophosphoric acid in 1:3 molar ratio have been carried out in refluxing, dry and distilled benzene. Water formed in the reaction has been fractionated out azeotropically.

$$3\ ROP(S)(SH)_2 + CrO_3 \xrightarrow{\text{Benzene}} Cr[S_2P(S)OR]_3 + 3H_2O$$

These reactions are completed in 8-10 hrs. Water molecules are removed azeotropically with benzene. The products are isolated as brown coloured powdery solids, washed 3-4 time with acetone and n-hexane and then dried. The compounds are soluble in organic solvents like ethanol, chloroform, DMF, DMSO etc.

Table 1 Synthetic and Analytic Data of $Cr[ROP(S)S_2]_3$

t	Reactant .....g;...(mmol)		Product		Analysis % found (clacd.)			
	CrO_3	$ROPSS_2$ R = ..	....g	...%..	C	H	S	Mol. Weight found (calcd.)
1.	0.4162 [4.1624]	CH_3 2.0000 [12.4879]	$Cr[CH_3OP(S)S_2]_3$ 5.95	91	6.63 (6.83)	1.61 (1.70)	53.20 (54.80)	526.01 (526.13)
2.	0.3827 [3.8273]	C_2H_5 2.0001 [11.4843]	$Cr[C_2H_5OP(S)S_2]_3$ 5.89	90	11.02 (12.66)	1.99 (2.63)	49.02 (50.75)	
3.	0.1771 [1.7711]	$^iC_3H_7$ 1.0001 [5.3147]	$Cr[^iC_3H_7OP(S)S_2]_3$ 2.89	89	16.54 (17.68)	2.30 (3.43)	46.98 (47.26)	
4.	0.1648 [1.6481]	$^iC_4H_9$ 1.0814 [4.9567]	$Cr[^iC_4H_9OP(S)S_2]_3$ 2.98	92	21.89 (22.06)	4.00 (4.13)	44.00 (44.21)	
5.	0.3000 [3.0017]	C_6H_5 2.000 [9.0021]	$Cr[C_6H_5OP(S)S_2]_3$ 5.79	90	29.01 (30.31)	1.82 (2.10)	39.77 (44.49)	
6.	0.2825 [2.8525]	o-$CH_3C_6H_4$ 2.0023 [8.4778]	$Cr[o\text{-}CH_3C_6H_4OP(S)S_2]_3$ 5.70	89	32.50 (3.39)	2.01 (2.78)	37.04 (38.24)	

IR Spectra

In the region of 4000-200 cm^{-1} (Table-2) IR spectra are recorded.

Following characteristic changes are observed

1. The υ(P)-O-C and υP-O-(C) linkage are present in the region 1054 – 1030 cm^{-1} and 898-833 cm^{-1} respectively.
2. The υP= S and υP-S linkage are present in the region 786 - 746 cm^{-1} and 631 - 597 cm^{-1} respectively.
3. The absorption band at 786 cm^{-1} and 631 cm^{-1} are assigned to υP= S and υP-S linkage, respectively. Shifting of bands towards lower frequency (30-40 cm^{-1}) from parent trithiophosphate indicates strong chelation of thiophosphoryl group to metal atom and also indicates the bidentate nature of this group.
4. A new medium and strong intensity absorption band of chromium- sulphur bond in 531- 504. cm^{-1} region.

Table 2 IR spectra data of $Cr[ROP(S)S_2]_3$

S.No.	Compounds	υ[(P)-O-C]	υ[P-O-(C)]	υ (P=S)	υ(P-S)	υ(Cr-S)
1.	$Cr[CH_3OP(S)S_2]_3$	1045 br	833 s	781 s	597 s	504 s
2.	$Cr[C_2H_5OP(S)S_2]_3$	1054 br	873 s	786 s	603 s	528 s
3.	$Cr[^iC_3H_7OP(S)S_2]_3$	1030 br	880 s	775 s	599 s	526 s
4.	$Cr[^iC_4H_9OP(S)S_2]_3$	1033 br	878 vs	746 s	605 m	510 s
5.	$Cr[C_6H_5OP(S)S_2]_3$	1042 br	898 s	756 s	621 m	531 s
6.	$Cr[o\text{-}CH_3C_6H_4OP(S)S_2]_3$	1047 br	860 s	779 s	631 s	508 s

br = broad vs = very sharp s = sharp m = medium

NMR Spectra

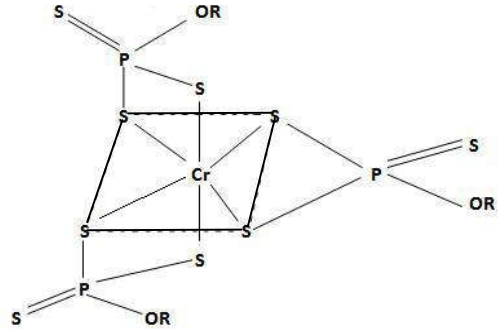
^{1}H NMR spectra:- The PMR spectra are recorded in 400 MHz region. The characteristic singnals due to alkoxy and phenyl protons (Table-3). The characteristic resonance singnals due to OCH_3, OCH_2, OCH, OC_6H_5 protons are present in the expected region.

^{31}P NMR Spectra:- ^{31}P NMR spectra are recorded in 121.49 MHz region. Proton decoupled ^{31}P NMR spectra observed in the region 108.40-98.90ppm show the deshielding of the phosphorus atom to the extent of about 36-26ppm from the parent trithiophosphoric ligand (Table-3). This indicates of a bidentate mode of bonding of the ligand moiety in these complexes.

On the basis of above studies octahedral geometry of O-alkyl/O-aryl trithiophosphate derivatives of chromium has been suggested, which consists with six coordinated chromium and bidentate behaviour of the trithiophosphate moiety.

Table 3 ^{1}H NMR spectra and ^{31}P NMR spectra of $Cr[ROP(S)S_2]_3$

S. No.	Compounds	^{1}H chemical shift (δ-ppm)	^{31}P Chemical shift (δ-ppm)
1.	$Cr[CH_3OP(S)S_2]_3$	2.04, s, 9H (OCH_3)	108.40
2.	$Cr[C_2H_5OP(S)S_2]_3$	1.97, t, 9H (CH_3) 2.80, q, 6H (OCH_2)	105.80
3.	$Cr[^iC_3H_7OP(S)S_2]_3$	1.89, d, 18H (CH_3) 2.95-3.09, m (OCH)	101.62
4.	$Cr[^iC_4H_9OP(S)S_2]_3$	1.44, d, 18H (CH_3) 2.22-2.14, m, 3H (CH) 2.84, d, 6H (OCH_2)	98.90
5.	$Cr[C_6H_5OP(S)S_2]_3$	6.36-6.72, m, 15H (OC_6H_5)	106.64
6.	$Cr[o\text{-}CH_3C_6H_4OP(S)S_2]_3$	6.48-6.82, m, 12H (C_6H_4) 1.92, s, 9H (CH_3)	107.31



CONCLUSION

On the basis of physio-chemical and spectroscopic data the structure of these complexes may be as follow:-

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