O,O'-Ditolyldithiophosphates of Zinc(II), Cadmium(II) and Mercury(II)

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ABSTRACT

O,O'-Ditolyldithiophosphato complexes of zinc(II), cadmium(II) and mercury(II) corresponding to $[(CreO)_2PS_2]_2M$ (CreO = *o*-, *m*- and *p*-$CH_3C_6H_4$ and M = Zn, Cd and Hg) have been synthesized by the reaction of metal dichlorides, MCl_2, with triethylammonium *O,O'*-ditolylphosphorodithioate, (*o*-, *m*- and *p*-$CH_3C_6H_4O)_2PS_2HNEt_3$, in 1:2 molar stoichiometry under anhydrous conditions. These complexes were characterized by elemental analyses, molecular weight determination, IR and NMR (^1H, ^{13}C and ^{31}P) spectral studies, which revealed monomeric nature of these complexes and the metal atom being four-coordinatively bonded to two bidentate dithiophosphate ligands, leading to a square plannar geometry around the metal atom.

$$MCl_2 + (CreO)_2PS_2HNEt_3 \xrightarrow[\text{Refluxing 4-7 Hrs}]{\text{Toluene}} [(CreO)_2PS_2]_2M$$
$$-Et_3NHCl$$

(M = Zn, Cd and Hg; Cre = *o*-, *m*- or *p*-$C_6H_4CH_3$)

Key words: Metallo-organic; Phosphorus compounds; Ditolyldithiophosphates; Dialkyl-/alkylenedithiophosphates

INTRODUCTION

Synthesis and various physico-chemical properties of dithiophosphates, of transition as well as main group elements, have been extensively investigated /1-3/. A structural variety of transition metal complexes with dithiophosphates has been explained in terms of coordination chemistry by the ability of these compounds to perform different functions and act as monodentate, bidentate (terminal and bridging) or

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chelating ligands. As a result, mono-, bi-, tetra- and in the general case, polynuclear complexes can be formed /4-6/. Dithiophosphato derivatives have significant properties and are efficiently used in technological and agricultural fields as antioxidants for lubrication oils /7-9/, flotation agents for mineral ores /10/, solvent extraction agents for metal cations /11/, polymerization catalysts /12/, acaricides, insecticides and pesticides /13-14/. Some of the organometallic derivatives have been found to display antitumor activity /15/. A literature survey revealed that sulfur ligands are especially important for zinc, cadmium and mercury because of the biological importance of these elements. Zinc is one of the most biologically important metals and is apparently necessary to all forms of life. The two zinc enzymes, particularly carboxypeptidase and carbonic anhydrase have received the highest attention /16/. Carbonic anhydrase is widely distributed both in plants and animals in several forms. Zinc complexes have been long used as catalyst /17/ and as fungicides /18/. In continuously variable ratio transmissions, high friction is a sought-after feature and ZDDPs are used to provide the same /19/. Phosphorodithioates of zinc are widely used as antioxidant and antiwear lubricants as well as vulcanization accelerators /8-9, 20/ and as such have received much attention.

On the other hand, cadmium and mercury are amongst the most toxic elements. Cadmium is extremely toxic and accumulates in humans, mainly in kidneys and liver /21/.The mobilization and immobilization of cadmium in the environment, in organisms, and in some technical processes (such as in ligand exchange chromatography) have been shown to depend significantly on the complexation of the metal center by chelating ligands /22/. The history of toxic effects of mercury is long known and the use of $HgCl_2$ as poison is well known /23/. In view of the above interesting facets, it was thought worthy to investigate the chemistry of these elements with *o-*, *m-* and *p*-ditolyldithiophosphates, and we report herein on the synthesis and characterization of some new *O,O'*-ditolyldithiophosphates of zinc(II), cadmium(II) and mercury(II).

EXPERIMENTAL

Materials and methods

Moisture was carefully excluded throughout the experimental manipulations by using standard Schlenk's techniques. All glassware was dried in a preheated oven. Toluene was dried by refluxing over sodium. The triethylammonium *O,O'*-bis(*ortho-*, *meta-* and *para-*)ditolylphosphorodithioates were prepared by the literature method /24/. Carbon and hydrogen were analyzed by on Vario EL III elemental analyzer. Sulfur was estimated as $BaSO_4$ (Messenger's method). Zinc, cadmium and mercury were estimated gravimetrically as zinc ammonium phosphate or pyrophosphate, dipyridinecadmium thiocyanate and mercury(II) sulfide, respectively /25/. Molecular weights were determined using cryoscopy in freezing benzene. IR spectra were recorded in nujol mulls in the range 4000–400 cm^{-1} on a Perkin Elmer- 377 or Brucker Vector 22 spectrophotometer. The ^1H, ^{13}C and ^{31}P NMR spectra were recorded on a Bruker DRX 300 (120 MHz) spectrometer, using TMS as the internal reference for ^1H NMR and 85% H_3PO_4 as an external reference for ^{31}P NMR.

Preparation of the compounds

[(*o*-$CH_3C_6H_2O)_2PS_2]_2Zn$ (1)

To a toluene suspension (~30 ml) of triethylammonium *O,O'*-(*ortho*-ditolylphosphorodithioate, (*o*-$CH_3C_6H_2O)_2PS_2HNEt_3$, (4.59 g/1.11 mmol) was added $ZnCl_2$ (0.75 g/0.55 mmol) with constant stirring at room temperature. The contents were then refluxed for 6 hours. The $ZnCl_2$ starts dissolving slowly and most of the $ZnCl_2$ was dissolved during this period. Now the contents were allowed to come to the room temperature, then the precipitates of Et_3NHCl were removed by means of a funnel fitted with G-4 sintered disc. The excess of solvent from the filtrate was evaporated under reduced pressure, which yielded the complex [(*o*-$CH_3C_6H_2O)_2PS_2]_2Zn$ (1) as colorless viscous product in 87% yield. Finally, the complex was washed with CCl_4 and dried in *vacuo*.

Similar procedure and stoichiometry was employed for the synthesis of all other complexes (2-9) except different refluxing period (4-7hours). The synthetic and analytical data of all the complexes are summarized in Table 1.

Note: Due to the poisonous nature of $CdCl_2$ and $HgCl_2$ all precautions were taken such as fuming hood, laboratory spectacle, hand gloves etc. were the integral component during experimental manipulations.

Table 1

Synthetic and analytical data of ditolylphosphorodithioates of Zn(II), Cd(II) and Hg(II).

S. No.	Reactants g (mmol) $LHNEt_3$	Reactants g (mmol) MCl_2	Compound* (Yield %)	M.W. Found (Calcd.)	Analysis (%) Found (Calcd.) C	H	S	M**
1.	4.59 (1.11)	0.75 (0.55)	[(*o*-$CH_3C_6H_4O)_2PS_2]_2Zn$ (87)	699.38 (684.98)	41.02 (41.16)	4.08 (4.13)	17.96 (18.75)	9.25 (9.56)
2.	4.84 (1.17)	0.79 (0.58)	[(*m*-$CH_3C_6H_4O)_2PS_2]_2Zn$ (86)	702.11 (684.98)	40.92 (41.16)	4.02 (4.13)	18.67 (18.75)	9.41 (9.56
3.	4.28 (1.04)	0.70 (0.51)	[(*p*-$CH_3C_6H_4O)_2PS_2]_2Zn$ (85)	708.19 (684.98)	41.08 (41.16)	4.04 (4.13)	18.45 (18.75)	9.37 (9.56)
4.	5.11 (1.24)	1.13 (0.61)	[(*o*-$CH_3C_6H_4O)_2PS_2]_2Cd$ (83)	752.10 (731.14)	45.79 (46.00)	3.76 (3.86)	17.35 (17.54)	14.96 (15.37)
5.	3.41 (0.83)	0.75 (0.41)	[(*m*-$CH_3C_6H_4O)_2PS_2]_2Cd$ (85)	754.12 (731.14)	45.84 (46.00)	3.74 (3.86)	17.15 (17.54)	15.06 (15.37)
6.	3.66 (0.89)	0.81 (0.44)	[(*p*-$CH_3C_6H_4O)_2PS_2]_2Cd$ (87)	750.19 (731.14)	45.82 (46.00)	3.64 (3.86)	17.22 (17.54)	14.94 (15.37)
7.	2.44 (0.59)	0.81 (0.29)	[(*o*-$CH_3C_6H_4O)_2PS_2]_2Hg$ (81)	839.10 (819.32)	40.92 (41.05)	3.26 (3.44)	14.96 (15.65)	23.95 (24.48)
8.	4.04 (0.98)	1.32 (0.48)	[(*m*-$CH_3C_6H_4O)_2PS_2]_2Hg$ (84)	841.12 (819.32)	40.56 (41.05)	3.24 (3.44)	15.46 (15.65)	24.15 (24.48)
9.	3.00 (0.73)	0.99 (0.36)	[(*p*-$CH_3C_6H_4O)_2PS_2]_2Hg$ (89)	840.10 (819.32)	40.88 (41.05)	3.12 (3.44)	15.35 (15.65)	23.96 (24.48)

*Compounds (1-3) are colorless viscous while all other compounds (4-9) are yellow viscous; **M = Zn (1-3), Cd (4-6) and Hg (7-9).

RESULTS AND DISCUSSION

Reactions of MCl_2 (M = Zn, Cd and Hg) with triethylammonium *O,O'*-ditolylphosphorodithioate, (*o*-, *m*- and *p*-$CH_3C_6H_4O)_2PS_2HNEt_3$, were carried out in 1:2 molar ratio in refluxing toluene under anhydrous and dinitrogen atmosphere, which yielded the complexes [(*o*-, *m*- and *p*-$CH_3C_6H_4O)_2PS_2]_2M$ (Scheme 1).

$$MCl_2 + (CreO)_2PS_2HNEt_3 \xrightarrow[\text{Refluxing 4-7 hours}]{\text{Toluene}} [(CreO)_2PS_2]_2M$$
$$-Et_3NHCl$$

Scheme 1: Reaction of MCl_2 with $(CreO)_2PS_2HNEt_3$, where M = Zn, Cd and Hg; Cre = *o*-, *m*- or *p*-$C_6H_4CH_3$

These reactions appeared a bit sluggish at room temperature and needed to be refluxed for 4-7 hours. The complexes were obtained as colorless or yellowish viscous liquid and were soluble in chloroform, dichloromethane, benzene, while insoluble in *n*-hexane and petroleum ether. These complexes appeared to be moisture sensitive. However, they can be kept unchanged for long periods under anhydrous and inert atmosphere. These compounds are non-volatile even under reduced pressure and get decomposed to a dark brown material, which could not be characterized. The outcome of the elemental analyses (C, H, S and M) did support the composition of individual complexes. The complexes are monomeric in nature as established by their molecular weight determination using cryoscopy.

Infrared spectra

The infrared spectra of these complexes have shown characteristic absorption for ν(P)–O–C in the region 1190-1118 cm^{-1} and the appearance of weak to medium intensity bands in the region 950–884 cm^{-1} were due to νP–O–(C) ring vibrations. The characteristic absorptions for νP=S and νP–S (symmetric and asymmetric vibrations) were observed with a slight shift compared to the parent dithiophosphate ligands in the region 779-668 cm^{-1} and 612-508 cm^{-1}, which is indicative of complexation between metal and ligand. The appearance of new bands in the region 469–443 cm^{-1} is also suggestive of νM–S bond formation. The relevant infrared spectral data are summarized in Table 2.

^{1}H NMR spectra

The ^{1}H NMR spectra of these complexes (in $CDCl_3$) have shown the characteristic resonance pattern for each proton. The chemical shift for the methyl protons was observed as singlet at 2.1-2.3 ppm. The aromatic protons of tolyl ring resonate as a multiplet in the range 7.0-7.9 ppm. The absence of methyl and methylene protons of the triethylamine moiety in the spectra of these complexes is indicative of formation of M-S bond as a consequence of removal of both chlorine atoms attached to the metal as Et_3NHCl. The ^{1}H NMR spectral data have been given in Table 3.

Table 2

IR spectral data of ditolylphosphorodithioates of Zn(II), Cd(II) and Hg(II) (in cm^{-1}).

Compound No.	(P)-O-C	P-O-(C)	P-S	P=S	M-S
1.	1166, vs	921, vs	598, m	760, s	443, m
2.	1152, vs	942, s	608, m	770, s	445, m
3.	1121, vs	950, s	612, m	779, s	450, m
4.	1169, s	914, s	557, m	671, s	443, m
5.	1175, s	911, s	580, m	692, s	449, m
6.	1190, s	905, s	596, m	694, s	469, m
7.	1118, s	932, s	532, m	648, s	447, m
8.	1135, vs	895, s	508, m	666, s	445, m
9.	1180, vs	884, s	570, m	680, s	461, m

Where vs = very strong, s = strong and m = medium.

^{31}P NMR spectra

The ^{31}P NMR spectra (proton decoupled) of all the complexes have shown the presence of chemical shift as singlet in each case, with a downfield shift compared to the parent dithiophosphato ligand. The chemical shift for these compounds was found in the region 80.0-83.0 ppm. Occurrence of singlet in each case might be correlated with the equivalent nature of phosphorus nucleus and symmetric nature of the species as well. The ^{31}P NMR spectral data are given in Table 3.

Table 3

^{1}H and ^{31}P NMR spectral data of ditolylphosphorodithioates of Zn(II), Cd(II) and Hg(II) in $CDCl_3$ (in ppm).

S. No.	^{1}H NMR	^{31}P NMR
1.	2.3, s, 6H ($-CH_3$); 7.2-7.7, m 8H ($-C_6H_4$)	80.2
2.	2.1, s, 6H ($-CH_3$); 7.1-7.6, m 8H ($-C_6H_4$)	80.8
3.	2.3, s, 6H ($-CH_3$); 7.2-7.7, m 8H ($-C_6H_4$)	83.0
4.	2.3, s, 6H ($-CH_3$); 7.2-7.7, m 8H ($-C_6H_4$)	81.4
5.	2.2, s, 6H ($-CH_3$); 7.0-7.6, m 8H ($-C_6H_4$)	80.1
6.	2.3, s, 6H ($-CH_3$); 7.2-7.7, m 8H ($-C_6H_4$)	82.0
7.	2.1, s, 6H ($-CH_3$); 7.2-7.7, m 8H ($-C_6H_4$)	80.0
8.	2.3, s, 6H ($-CH_3$); 7.3-7.8, m 8H ($-C_6H_4$)	81.4
9.	2.3, s, 6H ($-CH_3$); 7.4-7.9, m 8H ($-C_6H_4$)	82.4

Where s = singlet and m = multiplet

^{13}C NMR spectra

The ^{13}C NMR spectral data ($CDCl_3$) of these compounds have shown the resonance for methyl carbon in the region 18.7-22.9 ppm. The carbon nuclei of the tolyl ring showed their characteristic chemical shifts depending upon the location of the methyl group, whether *ortho-*, *meta-* or *para-*. The *ortho-* and *meta-* complexes gave six signals for phenylic carbon nuclei while four chemical shifts were found for *para-* derivatives. The chemical shift for –CO (C1) was observed in the range 155.4-157.7 ppm in these complexes. The chemical shift for methyl substituted carbon of the phenyl ring in *ortho-* (C 2), *meta-* (C 3) and *para-* C(4) was found in the region 122.4-122.9 ppm, 141.3-142.6 ppm and 132.8-133.6 ppm, respectively. The downfield swing in the chemical shift of $-C(CH_3)$ carbon in *meta-* and *para-* derivatives may be attributed to the presence of some hydrogen interactions in these complexes between proton attached to *ortho-* carbon of one tolyl ring and the oxygen atom of the other tolyl ring. In case of *para-* derivatives (**3**, **6**, **9**), only one chemical shift was observed each for C2, 6 and C3, 5 at 116.0-116.3 ppm and 132.6-133.0 ppm, respectively, while individual chemical shift was observed for each carbon in *ortho-* and *para-* complexes. The absence of the chemical shifts for the carbons of triethylamine moiety is also an indication of formation of these complexes. The ^{13}C NMR spectra data for a few representative complexes have been summarized in Table 4.

Structural features

It has been established that steric factors are associated with the dithiophosphate bound alkyl/aryl and/or the other groups attached to the zinc atom. The related cadmium dithiophosphates led to similar conclusions to those noted for zinc dithiophosphates /26/. Therefore in conjunction with the various physico-chemical studies like elemental analyses (C, H, S and M), molecular weight determination and spectral studies such as IR and NMR (^1H, ^{13}C and ^{31}P) and literature reports /12, 26/, a chelating four-coordinated square planar geometry may tentatively be proposed for these complexes (Figure 1).

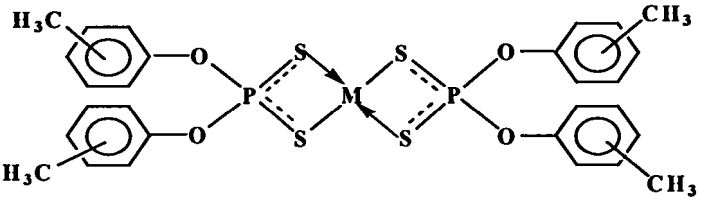
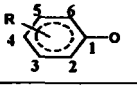


Fig. 1: Proposed square planar geometry for the complexes $[(o\text{-}, m\text{-} \text{ or } p\text{-}CH_3C_6H_4O)_2PS_2]_2M$; where M = Zn, Cd and Hg.

Table 4

^{13}C NMR spectral data of ditolylphosphorodithioates of Zn(II), Cd(II) and Hg(II) (in ppm).

S. No.	CH_3	 (Phenylic Carbon)
1.	18.7	55.5 C (1), 122.9 C (2), 133.6 C (3), 124.4 C (4), 130.3 C (5), 117.6 C (6)
2.	22.6	56.4 C (1), 142.8 C (2), 133.6 C (3), 124.5 C(4), 130.3 C (5), 117.7 C (6)
3.	19.2	155.6 C (1), 116.2 C (2) and C (6), 132.8 C (3) and C(5), 132.1 C (4)
4.	19.0	155.5 C (1), 122.8 C (2), 133.9 C (3), 124.8 C (4), 130.2 C (5), 117.8 C (6)
5.	22.9	157.7 C (1), 114.0 C (2), 141.3 C (3), 126.0 C (4), 128.8 C (5), 113.7 C (6)
6.	19.2	155.8 C (1), 116.3 C (2) and C (6), 133.0 C (3) and C(5), 132.4 C (4)
7.	18.8	155.4 C (1), 122.4 C (2), 133.4 C (3), 131.9 C (4), 132.6 C (5), 117.8 C (6)
8.	22.9	157.5 C (1), 115.2 C (2), 141.3 C (3), 126.4 C (4), 128.9 C (5), 113.8 C (6)
9.	19.0	155.6 C (1), 116.0 C (2) and C (6), 132.6 C (3) and C(5), 132.1 C (4)

ACKNOWLEDGEMENTS

One of the authors (S. K. Pandey) is thankful to the University Grants Commission, New Delhi, for financial support. The authors are grateful to Central Drug Research Institute, Lucknow, for providing NMR spectral studies.

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