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Synthesis and characterization of triarylphosphine complexes of zinc(II) halides

Ashok K. S. Chauhan*, Narendra Singh and Ramesh C. Srivastava

Chemistry Department, Lucknow University, Lucknow 226007, India

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Both 1 : 1 and 1 : 2 complexes are formed by zinc(II) halides and triarylphosphines unless electronic and/or steric factors intervene. Tri-*p*-chlorophosphine (a weaker base than PPh_3) forms only a 1 : 1 complex, whereas bulky tri-(ortho-substituted phenyl)phosphines do not react. The complexes ZnX_2PR_3 and $ZnX_2(PR_3)_2$ have been characterized by elemental analyses, conductance, far-IR and (in a few cases) Raman spectral studies. The Zn–X and Zn–P stretching and Zn–X bending vibrational frequencies have been assigned in the complexes with a pseudo-tetrahedral structure of C_{2v} symmetry.

KEYWORDS: triarylphosphine complexes; far IR–Raman frequencies; zinc(II) halide complexes; Zn–P stretching frequencies; ν(Zn–X)/ν(Zn–X′) ratios

INTRODUCTION

Among d^{10} metals, the tertiary phosphine complexes of cadmium and mercury have been studied in detail because of interest in the coupling constants $J(^{31}P-^{113}Cd)$, $J(^{31}P-^{111}Cd)$ and $J(^{31}P-^{199}Hg)$ that have been used as a tool to examine the effects of electronic and steric factors in the triarylphosphine complexes of these metals.[1–7] Although mercury(II) halides are known to form a wide range of stoichiometries with tertiary phosphine ligands, the 1 : 1 and 1 : 2 ($MX_2 : PR_3$) complexes are by far the most common.[8] Cadmium(II) halides, on the other hand, give mainly 1 : 2 complexes with tertiaryphosphines,[2–5] except with the phosphines that possess a large cone angle, such as tri-t-butylphosphine[9] and tricyclohexylphosphine,[10] which form 1 : 1 complexes only.

Studies on the complexes of zinc(II) with the phosphorus-donors are limited to triphenylphosphine[11–15] complexes of zinc(II) halides and to tri-t-butylphosphine complexes of zinc(II) halides and zinc(II) thiocyanate.[9] Whereas triphenylphosphine forms 1 : 2 complexes with zinc(II) halides, only 1 : 1 dimeric complexes are formed with tri-t-butylphosphine in aprotic solvents. In protic solvents or with hydrated zinc salts, anionic complexes of the type $(^tBu_3PH)^+$ $[Zn(P^tBu_3)X_3]^-$ (in 1-butanol) or $(^tBu_3PH)_2[Zn(NO_3)_3OH]$ (with $Zn(NO_3)_2 \cdot 6H_2O$) were obtained instead of neutral complexes.[9]

Although the effect of electronic and steric factors on the complexes of mercury(II) and cadmium(II) halides with various triarylphosphines has been examined,[1,3] no such studies with zinc(II) halide complexes seem to have been made. In this paper, the synthesis, characterization and spectral studies of triarylphosphine complexes of zinc(II) halides are described. Our objective was to evaluate the zinc–halogen and zinc–ligand stretching frequencies for isostructural complexes of different phosphines varying only in the electronic or steric environment at phosphorus. As the electronic effects of the para substituent can be transmitted across the ring to the phosphorus without substantially changing its steric requirement, complexes of para-substituted triarylphosphines were selected to study the electronic effects. Interactions of P(*o*-$MeC_6H_4)_3$ with zinc(II) halides were investigated to seek information on the steric effects.

MATERIALS AND METHODS

Triarylphosphines (from Strem Chemicals) were recrystallized before use. Anhydrous zinc(II) halides were reagent grade. Ethanol was refluxed over magnesium and distilled. Ether and hexane were dried over sodium and distilled before use. Dichloromethane (reagent grade) was distilled and stored over molecular sieves.

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*Correspondence to: Ashok K. S. Chauhan, Department of Chemistry, University of Lucknow, Lucknow 226007, India.
E-mail: akschauhan@hotmail.com

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Melting points were determined with a Gallenkamp melting point apparatus and are uncorrected. Carbon and hydrogen analyses were performed by Guelph Chemical Laboratories Ltd, Guelph, Canada and by RSIC, Central Drug Research Institute, Lucknow. Halide content was estimated gravimetrically. IR spectra were recorded with a Perkin–Elmer 180 spectrophotometer (University of Guelph, Canada) as Nujol mulls between polyethylene disks. Raman spectra (courtesy of Professor D. E. Irish) were measured in the solid state with a Jarrel–Ash spectrophotometer using the 5145 Å exciting line of an argon-ion laser.

Preparation of 1 : 1 complexes, ZnX_2PR_3

The phosphine (1 mmol) in diethyl ether (~20 ml) was added dropwise to anhydrous zinc halide (1 mmol) in the same solvent (~20 ml) with stirring at room temperature under an atmosphere of dry nitrogen. A white solid separated. After stirring the reaction mixture for 2 h to ensure completion of the reaction, the precipitated complex ZnX_2PR_3 was filtered, washed with diethyl ether (3 × 5 mL) and dried in vacuum. Yields were over 90%. The 1 : 1 complexes were almost insoluble in benzene, chloroform, and dichloromethane.

Preparation of 1 : 2 complexes, $ZnX_2(PR_3)_2$

A solution of the phosphine (2.10 mmol) in ethanol (~15 ml) was slowly added to anhydrous zinc halide (1 mmol) in the same solvent (~15 ml) at room temperature under an atmosphere of dry nitrogen. The resulting solution was stirred for about 5 h. A white solid that appeared on concentration and cooling of the solution was filtered and dried. It was recrystallized from a mixture of dichloromethane–hexane. Except for the losses during filtration and recrystallization, yields of the complexes were quantitative.

Attempted preparation of $ZnX_2[P(p\text{-}ClC_6H_4)_3]_2$

Zinc(II) chloride (0.14 g, 1 mmol) and the phosphine (0.80 g, 2.2 mmol) were stirred together in ethanol under dry nitrogen atmosphere for ~5 h. A white solid appeared, which was filtered, washed with ether (3 × 5 ml) and dried. The solid was characterized as the 1 : 1 complex $ZnCl_2P(p\text{-}ClC_6H_4)_3$ (authentic IR spectrum). Removal of the solvent from the filtrate afforded the unreacted phosphine (0.4 g). Zinc(II) bromide and zinc(II) iodide similarly afforded only 1 : 1 complexes with $P(p\text{-}ClC_6H_4)_3$.

Attempted reaction of zinc(II) bromide and $P(o\text{-}RC_6H_4)_3$

A solution of tri(*o*-tolyl)phosphine or tri(*o*-methoxyphenyl) phosphine (2.2 mmol) in ethanol was added to anhydrous zinc(II) bromide (1 mmol) in the same solvent. The reaction mixture was stirred for ~5 h. Removal of the solvent and extraction of the residue with petroleum ether left unreacted zinc(II) bromide as residue. The phosphine was recovered quantitatively from the extract after removing the petroleum ether under reduced pressure.

RESULTS AND DISCUSSION

Anhydrous zinc(II) halides react with triarylphosphines in diethyl ether in 1 : 1 molar ratio to give dimeric complexes $(ZnX_2PR_3)_2$. The 1 : 2 complexes, $ZnX_2(PR_3)_2$, are obtained when the halides are stirred with 2 mol of triarylphosphines in ethanol. The tendency to form 1 : 2 complexes is generally greater. As a result, analytically very pure samples of ZnI_2PR_3 (R = p-MeC_6H_4, p-$MeOC_6H_4$) could not be obtained due to the formation of the 1 : 2 complexes in small quantities as well. Repeated recrystallization appeared to increase the quantity of 1 : 2 complex. $P(p\text{-}ClC_6H_4)_3$, however, gave only 1 : 1 complexes with zinc(II) halides even in presence of an excess of the phosphine. Under similar conditions, $P(o\text{-}MeC_6H_4)_3$ failed to react with zinc(II) halides. $P(p\text{-}ClC_6H_4)_3$ is less basic than PPh_3, but $P(o\text{-}MeC_6H_4)_3$ is more basic. Thus, the instability of the 1 : 2 complex of $P(p\text{-}ClC_6H_4)_3$ with zinc(II) halides is probably due to electronic effects and that of $P(o\text{-}MeC_6H_4)_3$ due to steric reasons. Although mercury(II) halides are known to form 1 : 1 and 1 : 2 complexes with $P(p\text{-}ClC_6H_4)_3$, as well as a 1 : 1 complex with $P(o\text{-}MeC_6H_4)_3$,[4,5] the cadmium(II) halides do not react with either of the phosphines.[3] These observations suggest that the affinity of the halides of zinc(II), cadmium(II) and mercury(II) for tertiary phosphines varies in the series Cd < Zn < Hg.

All the compounds prepared in this study are air-stable white crystalline solids. The 1 : 2 complexes are soluble in polar organic solvents, but the 1 : 1 complexes are only sparingly soluble. Their melting points and analytical data are given in Table 1.

Vibrational spectra and structures

1 : 2 complexes

The Zn–X and Zn–P stretching frequencies and the Zn–X bending absorption frequencies for the complexes $ZnX_2(PPh_3)_2$ have been assigned in terms of molecular structure of C_{2v} symmetry.[11–15] Spectral data obtained in the present work also show that the 1 : 2 complexes of tri(para-substituted phenyl)phosphines reported herein are isostructural with the corresponding triphenylphosphine complexes. Since, for the isostructural complexes of a given phosphine, the Zn–X stretching and bending frequencies are expected to decrease with increasing mass of X, these frequencies can be assigned with reasonable certainty by comparing the spectra of the complexes with that of the free phosphine. The frequencies assigned are listed in Table 2.

For a pseudo tetrahedral complex of C_{2v} skeleton, X_2ZnP_2, both the symmetric and antisymmetric Zn–X stretching vibrations are active in the IR. The IR spectra of the complexes $ZnX_2(PR_3)_2$ showed two well-resolved bands attributable to the symmetric and antisymmetric Zn–X stretching frequencies. In each case the relative intensity of the higher frequency was markedly stronger and, therefore, was assigned to the antisymmetric stretching mode. This assignment is also supported by Raman spectra, where

Table 1. Analytical data for zinc(II) halide complexes of triarylphosphines

Complex $ZnX_2(PR_3)_n$				Elemental analysis Obs. (Calc.)	
X	*R*	*n*	M.p. (°C)	C (%)	H (%)
Cl	Ph	1	299 d	54.1 (54.3)	3.7 (3.8)
Cl	Ph	2	195	65.2 (65.4)	4.5 (4.6)
Br	Ph	1	315	44.2 (44.3)	3.1 (3.1)
Br	Ph	2	222	57.5 (57.7)	3.8 (4.0)
I	Ph	1	260 d	36.9 (37.2)	2.7 (2.6)
I	Ph	2	235–240	51.0 (51.3)	3.4 (3.6)
Cl	*p*-MeC_6H_4	1	290 d	57.0 (57.3)	4.6 (4.8)
Cl	*p*-MeC_6H_4	2	251	67.2 (67.7)	5.6 (5.7)
Br	*p*-MeC_6H_4	1	238	47.4 (47.6)	4.2 (4.0)[a]
Br	*p*-MeC_6H_4	2	234 d	60.2 (60.5)	5.0 (5.1)
I	*p*-MeC_6H_4	1	271 d	42.4 (40.5)	3.8 (3.4)
I	*p*-MeC_6H_4	2	250–255 d	54.1 (54.4)	4.7 (4.6)
Cl	*p*-$MeOC_6H_4$	1	211	51.3 (51.6)	4.2 (4.3)
Cl	*p*-$MeOC_6H_4$	2	209	60.3 (60.0)	5.1 (5.0)
Br	*p*-$MeOC_6H_4$	1	224	43.6 (43.7)	3.6 (3.7)
Br	*p*-$MeOC_6H_4$	2	216	54.1 (54.3)	4.3 (4.6)
I	*p*-$MeOC_6H_4$	1	176	38.8 (37.6)	3.9 (3.2)
I	*p*-$MeOC_6H_4$	2	160–164 d	49.5 (49.3)	4.2 (4.1)[b]
Cl	*p*-ClC_6H_4	1	266	42.7 (43.1)	2.8 (2.4)
Br	*p*-ClC_6H_4	1	285	37.0 (36.6)	2.3 (2.1)
I	*p*-ClC_6H_4	1	289 d	31.0 (31.6)	1.9 (1.8)

[a] Br: Obs. 29.89%, calc. for $C_{21}H_{21}Br_2PZn$, 30.25%.

[b] I: Obs. 24.46%, calc. for $C_{42}H_{36}I_2O_6P_2Zn$, 24.98%.

the higher frequency absorption due to the antisymmetric stretching mode is of weaker intensity. It can also be seen from Table 2 that frequency ratios ν(Zn–Br)/ν(Zn–Cl) and ν(Zn–I)/ν(Zn–Cl) for the antisymmetric stretching mode of Zn–X vibrations are also in excellent agreement with the reported frequency ratios for the $ZnX_2(PPh_3)_2$ complexes.[14] The X–Zn–X deformation frequencies for the substituted triarylphosphine complexes are similar to those observed for $ZnX_2(PPh_3)_2$.[12,13]

Zinc–phosphorus stretching frequencies have been reported to occur in the range of 166–153 cm^{-1} for $ZnX_2(PPh_3)_2$.[14] A medium-to-strong band in the 146–175 cm^{-1} region, assignable to the antisymmetric Zn–P stretching frequency, is observed in the complexes of triarylphosphines $ZnX_2(PR_3)_2$ prepared in this work. A medium-to-strong band in the 132–170 cm^{-1} region is also observed in the Raman spectra of the complexes examined (Table 2), which may be assigned to the Zn–P stretching mode. For a given phosphine, the ν(Zn–P) decreases slightly with increasing mass of X. Lewis acidity of ZnX_2 is also expected to decrease from X = Cl to X = I. However, significant variations are not observed in the Zn–P stretching frequencies of the complexes of various triarylphosphines with a given ZnX_2, showing that the effects of the subtle changes in the electronic environment of the phosphines are not amenable for study by IR spectroscopy.

1 : 1 complexes

As shown in Table 3, the 1 : 1 complexes of zinc(II) halides with triarylphosphines show three strong bands below the 400 cm^{-1} region. All these bands shift progressively to lower frequencies as X is changed from Cl to Br to I. Thus, there can be little doubt that these bands are associated with the vibrations of the metal–halogen bonds. For each complex, the highest frequency is comparable to the metal–halogen antisymmetric stretching frequency observed for the tetrahedral complexes $ZnX_2(PPh_3)_2$ or for $CdX_2(PPh_3)_2$,[14] and these can be assigned to the terminal Zn–X stretching frequency.

Little information is available in the literature on the bridged metal–halogen stretching frequencies for zinc. For the binuclear anion $[Zn_2Cl_6]^{2-}$, the IR bands at 238 and 225 cm^{-1} have been assigned to the bridged Zn–Cl stretching frequencies.[11] The remaining two strong bands can, therefore,

Table 2. Vibrational spectral data for 1 : 2 triarylphosphine complexes of zinc(II) halides

$ZnX_2(PR_3)_2$		ν(Zn–X) (cm^{1})		ν(Zn–X)/ ν(Zn–X′)		ν(Zn–P) (cm^{1})	
X	R	IR	Raman	ratio	δ(Zn–X) (cm^{1})	IR	Raman
Cl	Ph	318vs, 298s		Br/Cl 0.74	122m	168s	
Br	Ph	236vs, 205m	237sh, 204s	I/Cl 0.63	84mbr	160m	157w
I	Ph	199s, 174vs	200s, 174s		54m	152s	132s
Cl	*p*-MeC_6H_4	312vs, 292vs		Br/Cl 0.76	102s, 70w	168m	
Br	*p*-MeC_6H_4	237vs, 200vs	238s, 204vs	I/Cl 0.63	71s,52w	166s,154s	155s
I	*p*-MeC_6H_4	198vs, 169s[a]			71s, 62w		
Cl	*p*-$MeOC_6H_4$	310s, 290m,		Br/Cl 0.81	102m, 70m	156s	
Br	*p*-$MeOC_6H_4$	250vs, 205vs,		I/Cl 0.63	76m	157s	
I	*p*-$MeOC_6H_4$	194vs, 172vs			77m, 42sh	161m, 162m	

[a] Mixture of ν(Zn–I) and ν(Zn–P).

Table 3. Vibrational spectral data for 1 : 1 triarylphosphine complexes of zinc(II) halides

ZnX_2PR_3		ν(Zn–X) (cm^{-1})		ν_b(Zn–X)/ ν_t(Zn–X)	δ(Zn–X) (cm^{-1})	ν(Zn–P) (cm^{-1})	
X	R	IR	Raman			IR	Raman
Cl	Ph	334vs, 244sh, 230vs	340m, 270m	0.73	122s	167s	172m
Br	Ph	250vs, 188vs, 176vs	254vs, 188m	0.75	82m	150m	160s
I	Ph	212vs, 164vs, 157vs		0.77	68m		
Cl	p-MeC_6H_4	336vs, 250s, 222s		0.74	123s, 100w, 85w	174m	
Br	p-MeC_6H_4	241s, 202vs		0.83	72s, 53w	168s	
Cl	p-$MeOC_6H_4$	242vs, 202vs		0.83	54s	168s	
Br	p-$MeOC_6H_4$	212vs, 166vs, 158s		0.78	67m		
Cl	p-ClC_6H_4	340vs, 250vs, 234vs		0.72	113s, 71m	157s	
Br	p-ClC_6H_4	251vs, 192s, 170vs		0.77	82m, 72m	154m	
I	p-ClC_6H_4	214vs, 165vs, 156s		0.77	66m		

be assigned to bridged Zn–X stretching frequencies (Table 3). The ratio $\nu_b(M{-}X)/\nu_t(M{-}X)$ for $[Zn_2Cl_6]^{2-}$, Al_2X_6 and the dimeric square planar complexes $M_2X_4L_2$ (where M = Pt or Pd; X = Cl, I; L = PR_3) is reported[11,16,17] to vary from 0.63 to 0.83. As shown in Table 3, the $\nu_b(M{-}X)/\nu_t(M{-}X)$ ratios for the ZnX_2PR_3 complexes are in the range 0.72 to 0.83. Thus, the IR data for the 1:1 complexes of zinc(II) halides with triarylphosphines clearly show that these complexes contain terminal as well as bridging metal–halogen bonds. Like 1:2 complexes, all the 1:1 complexes prepared during the course of this investigation show a medium–strong band in 150 to 175 cm^{-1} range, which may be assigned to the stretching mode vibrations of the Zn–P linkage.

Although the 1:1 complexes of zinc(II) halides with triarylphosphines are not soluble enough for molecular weight measurements, a dimeric structure, similar to the complexes of tri-t-butylphosphine with zinc(II) halides[9] may be assigned on the basis of IR spectral data.

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REFERENCES

1. Bell NA. *Adv. Inorg. Chem. Radiochem.* 1972; **14**: 255.
2. Levason W, McAuliffe CA. *Coord. Chem. Rev.* 1976; **19**: 173.
3. Goel RG, Henry WP, Srivastava RC. *Inorg. Chem.* 1981; **20**: 1727 and references cited therein.
4. Alyea EC, Dias SA, Goel RG, Ogini WO, Pilon P, Merk DW. *Inorg. Chem.* 1978; **17**: 1697.
5. Goel RG, Henry WP, Ogini WO. *Can. J. Chem.* 1979; **57**: 762.
6. Bell NA, Goldstein M, Jones T, Nowell IW. *Inorg. Chim. Acta* 1983; **75**: 21.
7. Baker LJ, Bowmaker GA, Skelton BW, White AH. *J. Chem. Soc. Dalton Trans.* 1993; 3235.
8. Bell NA, Coles SJ, Hursthouse MB, Light ME, Malik KA, Mansor R. *Polyhedron* 2000; **19**: 1719 and references cited therein.
9. Goel RG, Ogini WO. *Inorg. Chem.* 1977; **16**: 1968.
10. Moers FG, Langhout JP. *Recl. Trav. Chim. Pays-Bas* 1973; **92**: 996.
11. Coates GE, Ridley D. *J. Chem. Soc.* 1964; 166.
12. Deacon GB, Green JHS. *Spectrochim. Acta Part A* 1968; **24**: 845.
13. Deacon GB, Green JHS. *Chem. Commun.* 1966; 629.
14. Deacon GB, Green JHS, Harrison DJ. *Spectrochim Acta Part A* 1968; **24**: 1921.
15. Bradbury J, Forest KP, Nuttall RH, Sharp DWA. *Spectrochim. Acta Part A* 1967; **23**: 2701.
16. Ferraro JR. *Low Frequency Vibrations of Inorganic and Coordination Compounds*. Plenum Press: New York, 1971; 177.
17. Alyea EC, Dias SA, Goel RG, Ogini WO. *Can. J. Chem.* 1977; **57**: 4227.