Asian Journal of Chemistry Vol. 7, No. 3 (1995), 471–474

Synthesis and Chracterization of some Mercury(II) Complexes with Phosphine Oxide, Sulphide and Mixed Ligands

SUBHI A. AL-JIBOURI, LAMA'AN J. AL-HAYALY
and
TALAL A.K. AL-ALLAF*
Department of Chemistry
College of Science, University of Salah Al-Din, Erbil, Iraq

A series of mercury(II) complexes of the general formula $HgX_2 \cdot L$ ($X = Cl^-$, Br^-, I^-; $L = (Ph_2PO)_2(CH_2)_n$, n = 1 or 2; $Ph_2(O)CH_2PPh_2$; $(Ph_2PS)_2(CH_2)_n$, n = 1, 2 or 3 and $Ph_2P(O)CH_2P(S)Ph_2$, have been prepared and characterized on the basis of their elemental analysis and IR spectroscopy.

INTRODUCTION

There is a considerable interest in the coordination properties of the bidentate ligands, methylenebis (diphenylphosphine oxide) and the corresponding sulphide and selenide with transition and non-transition metals[1]. The complexes of these ligands with cobalt(II), nickel(II), copper(II) and palladium(II)[1, 2] have been studied extensively. Additional related work has been carried out with iron(II), iron(III)[3, 4], chromium(0), molybdenum(0), tungsten(0)[5], uranium(VI)[6] and neodymium(III)[7]. Our recent work[8] on these ligands has dealt with non-transition metal, *i.e.*, tin. We investigated the reaction of these ligands with the organotin(IV) compounds R_xSnCl_{4-x}, (R = Me, Bu^n, Ph; x = 3, 2, 1 respectively) and found to behave as monodentate ligands in some cases and bidentate in other cases. However, very little work has been carried out on the coordination properties of phosphine oxide and sulphide with mercury[5, 9]. Therefore, in order to study the nature of interaction between P═O and P═S groups with Hg(II) halides and factors affecting such interaction, we reported here the synthesis and characterization of $HgX_2 \cdot L$ complexes, where $X = Cl^-$, Br^-, I^- and $L = (Ph_2PO)_2CH_2$, $dppmO_2$; $(Ph_2PO)_2(CH_2)_2$, $dppeO_2$; $Ph_2P(O)CH_2PPh_2$, dppmO; $(Ph_2PS)_2CH_2$, $dppmS_2$; $(Ph_2PS)_2(CH_2)_2$, $dppeS_2$; $(Ph_2PS)_2(CH_2)_3$, $dpppS_2$ and $Ph_2P(O)CH_2P(S)Ph_2$, dppmOS.

EXPERIMENTAL

IR spectra were recorded on a SP2000 spectrophotometer in the 4000–200 cm^{-1} range using Nujol mull and CsI discs.

Elemental analyses were performed in the laboratoris of Prof. Dr. W.P.

---

*Department of Chemistry, College of Science, University of Mosul, Mosul, Iraq.

Neumann, Dortmund University, FRG, Using a CHN Analyzer, type 1106 (Carlo Erba).

$HgCl_2$, $HgBr_2$ and HgI_2 were commercial products (Fluka) and they were used without further purfication. The $dppmO_2$, $dppeO_2$, dppmO, $dppmS_2$, $dppeS_2$, $dpppS_2$ and dppmOS ligands (L) were prepared according to standard methods[8, 10–12].

Preparation of the $HgX_2 \cdot L$ complexes

(1) *L* = *dppmO*$_2$, *X* = Cl^-, Br^-, I^-; *L* = *dppeO*$_2$, *dppmO, dppmOS, X* = Cl^-: A solution of the ligand (L) (1 mmol) in $CHCl_3$ (10 cm^3) was added to a solution of HgX_2 (1 mmol) in EtOH (10 cm^3). The mixture was heated under reflux on a steam bath for *ca.* 2.5 h, then cooled to room temperature. The reaction mixture was reduced in volume to *ca.* 10 cm^3 and either MeOH or *n*-hexane was added. The white solid product thus formed was filtered, washed with small protions of EtOH and *n*-hexane and dried under vacuum for several hrs. In the case of the $HgI_2 \cdot dppmO_2$ complex, upon filtration of the yellow solid, a rapid decomposition to red solid was observed, identified as HgI_2.

(2) *L* = *dppmS*$_2$, *dppeS*$_2$, *dpppS*$_2$; *X* = Cl^-, Br^-, I^-: A solution of the ligand (L) (1 mmol) in $CHCl_3$ (10 cm^3) was added to a solution of HgX_2 (1 mmol) in EtOH (10 cm^3) when X = Cl^- or Br^- and in MeOH (10 cm^3) when X = I^-. The mixture was heated under reflux on a steam bath for *ca.* 1 h to give the product as insoluble solid. This was filtered off, washed with small portions of $CHCl_3$, EtOH and *n*-hexane and dried over P_2O_5 under vacuum for several hrs.

RESULTS AND DISCUSSION

It has been found that $Ph_2P(O)CH_2PPh_2$(dppmO) reacts with HgX_2 (X = Cl^-, Br^-) to give complexes of the type $HgX_2 \cdot dppmO$ [5]. IR spectra of these complexes showed much smaller decrease in ν(P═O) (2–11 cm^{-1}) compared to the usual decrease (25–40 cm^{-1}) found in complexes of metal cations[1]. This has been explained as a combination of the normal drop in ν(P═O) on phosphoryl coordination and an increasc caused by a positive charge on the coordinated phosphine (pseudo-quaternization). It has also been concluded from IR and ^{31}P NMR that Hg(II) bonded strongly to phosphine than to phosphoryl[5].

This has led us to investigate the interaction of Hg(II) halides with ligands of the type $Ph_2P(O)(CH_2)_nP(O)Ph_2$ (n = 1 or 2), in which both phosphorous atoms are oxidized. We have also investigated here the interaction of Hg(II) halides with ligands of the type $Ph_2P(S)(CH_2)_nP(S)Ph_2$ (n = 1, 2 or 3) for commparison and $HgCl_2$ with $Ph_2P(S)CH_2P(O)Ph_2$ looking for the effects of P═O interaction with Hg(II), on P═S interaction with Hg(II). These complexes were isolated and identified by elemental analysis. IR spectroscopy and m.p., all data are given in Table-1.

TABLE-1
PHYSICAL PROPERTIES OF $HgX_2{\cdot}L$ COMPLEXES

L	X	Yield %	Colour	(m.p.) (°C)	% Analysis Found (Calcd.)		IR data (cm^{-1})	
					C	H	ν(P═O) (Δν)	ν(P═S) (Δν)
$dppmO_2$	Cl	82	white	150–152	b	b	1183 s, 1150 s (25), (40)	
	Br	77	white	152–153	39.6 (40.2)	3.1 (2.95)	1182 s, 1163 s (26), (27)	
$dppeO_2$	Cl	57	white	226–228	44.2 (44.5)	3.2 (3.4)	1185 m 1163 s (3), (13)	
dppmO	Cl	86	white	214–215	45.0 (44.7)	3.2 (3.3)	1179 s, — (6), —	
dppmOS	Cl	73	white	170–171	42.6 (42.6)	3.1 (3.1)	1180 s, — (12), —	574 s, (34)
$dppmS_2$	Cl	82	white	288 (dec.)	41.8 (41.7)	3.2 (3.1)		585 m, 568 s (37), (42)
	Br	98	white	248–249	37.5 (37.1)	3.0 (2.7)		590 w, 572 s (32), (38)
	I	80	off-white	210	33.5 (33.2)	2.4 (2.5)		588 w, 568 s (34), (42)
$dppeS_2$	Cl	93	white	205–206	42.8 (42.5)	3.3 (3.3)		584 s, 577 s (39), (33)
	Br	92	white	218–219	38.0 (37.95)	2.9 (2.9)		588 s, 578 s, (35), (32)
	I	83	pale-yellow	266	34.3 (34.05)	2.6 (2.6)		583 s, 575 s (40), (35)
$dpppS_2$	Cl[c]	81	white	253–255	37.8 (38.7)	3.0 (3.1)		582 s, 575 s (40), (30)
	Br[c]	77	white	235–240	35.7 (35.1)	2.9 (2.8)		582 s, 579 s (39), (26)
	I	82	off-white	203–205	34.8 (34.8)	2.7 (2.8)		586 s, 577 s (36), (28)

Δν calculated from ν (ligand)–ν (complex).
[b] Fairly satisfactory analyses were obtained.
[c] Complex solvated with one mole of $CHCl_3$.

Treatment of ($L = dppmO_2$ with HgX_2 ($X = Cl^-$ or Br^-) gave stable white solids, on the basis of elemental analysis, these complexes were formulated as $HgX_2{\cdot}L$. IR spectral data of the complexes showed a decrease in both ν(P═O) for about 25 cm^{-1}. This decrease is in good agreement with that listed in the literature, indicating that both P═O are coordinated. The stretching frequencies of Hg—X were too weak to be identified. On the other hand, treatment of HgI_2 with $dppmO_2$ gave yellow crystalline solid. On filtration in air, it decomposes rapidly to give red solid. From its colour and m.p., this solid was identified as the starting material (HgI_2).

$DppeO_2$ reacts similarly with $HgCl_2$ and $HgBr_2$ to give stable white solids. IR spectra showed much lower decrease in ν(P=O) (about 3–13 cm^{-1}) which suggest a weaker interaction of P=O with Hg(II). This is probably due to a larger size of the chelate ring compared to that with $dppmO_2$.

We have also attempted reactions of $Ph_2P(S)(CH_2)_nP(S)Ph_2$ (n = 1, 2 or 3) with HgX_2. Thus treatment of $dppmS_2$, $dppeS_2$ and $dpppS_2$ with HgX_2 ($X = Cl^-$, Br^- or I^-) gave white solids where $X = Cl^-$ or Br^- and yellow solid where $X = I^-$. These complexes were found to be highly insoluble in common organic solvents. On the basis of their elemental analyses, these complexes were again formulated as $HgX_2 \cdot L$. IR spectral data showed that on coordination, both ν(P=S) were lowered by *ca.* 32–40 cm^{-1} for $dppmS_2$ and $dppeS_2$. This value is in agreement with the reported value[9], and suggested that both P=S are coordinated. On the other hand, ν(P=S) values for $HgX_2 \cdot dpppS_2$ were lowered by 40, 29 and 26 cm^{-1} for $X = Cl^-$, Br^- and I^- respectively, which reflect the effects of type of halogen on P=S metal interaction.

Furthermore, in order to examine the effects of P=S group on the interaction of P=O with Hg(II). We have treated the dppmOS ligand with $HgCl_2$, a white solid was obtained, which gave a satisfactory elemental analyses for the formula $HgCl_2 \cdot dppmOS$. IR spectrum of this complex showed that both P=S and P=O are coordinated. ν(P=O) value (12 cm^{-1}) was much lower than the value obtained for $dppmO_2$ (25–40 cm^{-1}). This value suggests that P=O is weakly bonded to Hg(II). ν(P=S) however, was 34 cm^{-1}, almost similar to that found in the case of $dppmS_2$ (37 cm^{-1}).

REFERENCES

1. W.E. Slinkard and D.W. Meek, *J. Chem. Soc. Dalton*, 1973 (1973) and references therein.
2. Z.A. Sheka, K.B. Yatsimirskii, and M.A. Alova, *Russ. J. Inorg. Chem.*, **15**, 1526 (1970).
3. T.S. Lobana, H.S. Cheema and S.S. Sandhu, *Polyhedron*, **4**, 717 (1985).
4. ________, *Spectrochim. Acta*, **42A**, 735 (1986).
5. S.O. Grim, L.C. Satek, C.A. Tolman and J.P. Jesson, *Inorg. Chem.*, **14**, 656 (1975).
6. M.A. Wassef, W.S. Hegazi and S.A. Ali, *Egypt J. Chem.*, **26**, 197 (1983).
7. A.Z. Sheka and E.I. Sinyavskaya, *Russ. J. Inorg. Chem.*, **14**, 1093 (1969).
8. T.A.K. Al-Allaf, S.A. Al-Jibory and L.J. Al-Hayaly, *J. Iraqi Chem. Soc.* (in press).
9. T.S. Lobana and M.K. Sandhu, *Chem. and Indus.*, 106 (1986).
10. W. Hewertson and H.R. Watson, *J. Chem. Soc.*, 1490 (1962).
11. A.G. Abatjoglou and L.A. Kapicak (Union Carbide Group), *Europ. Pat. Appl. Ep.*, 72560 (Cl. CO7F 9/53), 23 Feb. 1983; US Appl. 293, 145, 17 Aug. 1981, 35 pp; *Chem. Abstr.*, **98**, 198452 p (1983).
12. S.O. Grim and E.D. Walton, *Inorg. Chem.*, **19**, 1982 (1980).

(*Received*: 4 July 1994; *Accepted*: 1 November 1994) AJC-892