ELSEVIER

Inorganica Chimica Acta 267 (1998) 169–172

Inorganica Chimica Acta

Note

Synthesis and NMR spectroscopy of dichlorobis(acetophenonethiosemicarbazone)mercury(II) formed from phenylmercury(II) chloride and acetophenonethiosemicarbazone: the first example of symmetrisation in organomercury(II)-thiosemicarbazone chemistry

T.S. Lobana *,[1], A. Sánchez, J.S. Casas *, M.S. García-Tasende, J. Sordo

Departamento de Química Inorgánica, Facultade de Farmacia, Universidade de Santiago de Compostela, 15706 Santiago de Compostela, Spain

Received 18 November 1996; revised 17 January 1997; accepted 19 March 1997

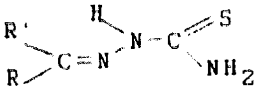
Abstract

The reaction of phenylmercury(II) chloride with acetophenonethiosemicarbazone (Hatsc) in ethanol in 1:1 mole ratio undergoes symmetrisation forming the products, $HgCl_2(Hatsc)_2$ and Ph_2Hg instead of the anticipated compound PhHgCl(Hatsc). The analytical data, some physical properties, IR and NMR (^1H, ^{13}C, ^{199}Hg) spectroscopy all support the formation of $HgCl_2(Hatsc)_2$. ^{199}Hg NMR of the solid obtained from the filtrate of the reaction provides evidence for Ph_2Hg. This reaction represents the first example of a symmetrisation phenomenon observed in organomercury(II)-thiosemicarbazone chemistry. © 1998 Elsevier Science S.A.

Keywords: Organomercury(II) complexes; Thiosemicarbazone complexes

1. Introduction

Organomercury(II) substrates, RHgX, are known to undergo symmetrisation forming symmetric diorganomercurials HgR_2 and Hg(II) complexes [1–3]. However, stabilisation of the dicoordinate $[PhHg(PPh_3)]^+$ [4] and tetracoordinate $[RHgL]^+$ species (R = Me, Ph; L = tripodal ligand, $N(CH_2CH_2PPh_2)_3$, coordinating via all three phosphorus atoms) [5] has been reported. No symmetrisation occurs with the analogous phosphine chalcogenides (Ph_3PE, E = O, S or Se) [3].



(I)

In order to understand the generality of the symmetrisation phenomenon, in this note, the reaction of phenylmercury(II) chloride with acetophenonethiosemicarbazone (I, Hatsc, $R' = CH_3$, $R = C_6H_5$, shown in the *E*-configuration) is described as an example of general symmetrisation reaction and the products identified using analytical data, some physical properties, IR and multinuclear (^1H, ^{13}C, ^{199}Hg) NMR spectroscopy. It may be noted that limited investigations on complexes of thiosemicarbazides and thiosemicarbazones with mercury(II) or organomercury(II) have been reported [6–10].

2. Experimental

2.1. Techniques used

The elemental analysis for C, H and N were obtained with a Carlo-Erba 1108 microanalyser. Melting points were determined with a Gallenkamp electrically heated apparatus. The IR spectra were recorded in KBr pellets (4000–400 cm^{-1}) or nujol mull in polyethene sheets (500–100 cm^{-1}) on a Bruker IFS 66V spectrometer. The NMR spectra were recorded in (i) $(CD_3)_2SO$ using a Bruker AMX 300 spectrometer at 300.14 and 75.48 MHz frequencies (^1H and ^{13}C) with TMS as the internal reference and (ii) $(CD_3)_2SO$ or $CDCl_3$ using a Bruker AMX 500 spectrometer at 89.51 MHz

---

* Corresponding author.

[1] Visiting Professor from Department of Chemistry, Guru Nanak Dev University, Amritsar 143005, Punjab, India (Feb. 1996–Apr. 1997).

PII S0020-1693(97)05574-6

probe frequency (^{199}Hg) with neat Me_2Hg as the external reference.

2.2. *Preparation of acetophenonethiosemicarbazone (Hatsc)*

This ligand was prepared by the methods reported for other related thiosemicarbazones [11] as follows. To thiosemicarbazide (3.65 g, 0.04 mol) suspended in 75 ml of distilled water was added about 2 ml of glacial acetic acid and the mixture was heated until a clear solution was formed. To this was added slowly under constant stirring acetophenone (5 ml, 0.04 mol) dissolved in 30 ml of ethanol. The contents were refluxed for a period of 6 h and, on cooling, a light yellow solid formed, which was filtered and dried in vacuo. Yield 70%; m.p. 114–115°C. IR data (cm^{-1}): 3408s, 3364m (νNH); 3236s, 3210s, 3147s (νCH + νNH); 1587vs, 1511vs, 1490vs (νC=N + νC=C + δNH_2); 1460s, 1444s (δCH); 1310sh, 1293s, 1105m (νN–N + νC–N); 1095s (νC=S); 964m (ρCH_3); 847s (νC=S); 764s, 752m (ring modes); 688s (δC=N, δC=C).

2.3. *Reaction of PhHgCl with Hatsc and synthesis of $HgCl_2(Hatsc)_2$ (compound A)*

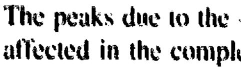
To a PhHgCl solution (0.313 g, 1 mmol) in 50 ml of ethanol was added the ligand solution (0.193 g, 1 mmol). The contents were stirred at room temperature (20–25°C) for a period of 48 h and the white solid formed was filtered, washed with ethanol and dried in vacuo. Yield 55%; m.p. 245–250°C (d). *Anal.* Found: C, 32.6; H, 3.4; N, 12.6. Calc. for $C_{18}H_{22}N_6S_2Cl_2Hg$: C, 32.8; H, 3.3; N, 12.8%. IR data (cm^{-1}) for $HgCl_2(Hatsc)_2$: 3386m, 3342w (νNH); 3267s, 3172s, 3056w (νCH + νNH); 1598vs, 1528vs, 1493vs (νC=N + νC=C + δNH_2); 1460sh, 1444m (δCH); 1296w, 1280s, br, 1097vw (νN–N + νC–N); 1088w (νC=S); 967w (ρCH_3); 834s (νC=S); 764s, 745m (ring modes); 686s (δC=N + δC=C); 388m (νHg–S); 342m (νHg–Cl). A new solid (compound **B**) obtained from the filtrate after evaporating all the solvent at room temperature was used for recording its ^{199}Hg NMR spectrum in order to confirm the formation of Ph_2Hg in the symmetrisation reaction.

3. Results and discussion

The analytical data of the white solid, obtained from the reaction of phenylmercury(II) chloride with acetophenonethiosemicarbazone (Hatsc), reveal the formation of $HgCl_2(Hatsc)_2$ (compound **A**), instead of the anticipated PhHgCl(Hatsc) compound. Product **A** is a high melting white solid which decomposes at 245–250°C to a black mass. It is soluble in DMSO and DMF, but virtually insoluble in all other solvents and repeated efforts to grow crystals of complex **A** were in vain.

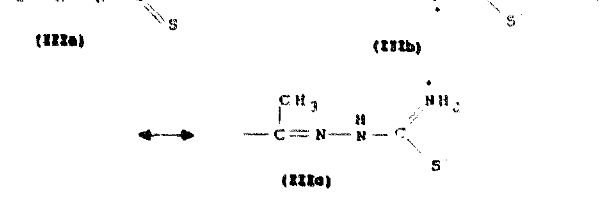
In the IR spectrum of **A**, the ν(NH) bands due to the $-N^1H_2$ and $-N_2H$ groups undergo changes to low energy, but are not sufficient to suggest coordination by the NH_2 group in accordance with its non-participation in bonding to metals [6,11,12]. The coordination of sulfur to Hg(II) is clearly shown by (i) a new characteristic peak at 388 cm^{-1} due to ν(Hg–S) and (ii) to the shift in the strong peak due to ν(C=S) at 847 cm^{-1} in the free Hatsc to 843 cm^{-1} in the complex. The ν(Hg–Cl) band occurs at 342 cm^{-1} in its characteristic region but the bands due to ν(C=N), ν(C=C) and $\delta(NH_2)$ are difficult to assign separately and are thus assigned as overlapping bands in the 1490–1600 cm^{-1} region [3,11–13].

The $-N^2H-$ group of Hatsc is not deprotonated in complex **A** but shifts to low field as shown by its ^{1}H NMR data (Table 1). Similarly, the $-N^1H_2$ protons appear as sharp and strong signals at low-field positions in this complex. Two peaks due to the $-N^1H_2$ protons in Hatsc and complex **A** are probably due to the restricted rotation of this group about the C^1–N^1 bond axis due to the partial double bond character and the low-field shift of the $-NH_2$ protons reveals deshielding of these protons with the possibility of enhanced double bond character in the C^1–N^1 bond in complex **A**. The $-CH_3$ group attached to the C^2 carbon undergoes a low-field shift by 0.12 ppm, but the $-C_6H_5$ signals are nearly unaffected in the complex; the above changes clearly support coordination by thione sulfur of the neutral Hatsc to the Hg(II) centre (**I**, *E*-configuration). It may be noted that coordination of a thiosemicarbazone in the deprotonated form (**II**, *Z*-configuration) leads to an upfield shift in the ^{1}H(N^1H_2) signals [11,14]. Thus, ^{1}H NMR data unequivocally confirm coordination of Hatsc to Hg(II) via its thione sulfur in the neutral form.



(II)

In the ^{13}C NMR spectrum of Hatsc (Table 1), the $^{13}C^1$ NMR signal at δ 179.1 shows a high-field shift, while the $^{13}C^2$ and $^{13}C^0$ signals in complex **A** undergo low-field shifts. The peaks due to the $-C_6H_5$ group of Hatsc are marginally affected in the complex. Thus, coordination via the thione sulfur leads to shielding of the C^1 carbon and deshielding of the C^2 and C^0 carbons. The shielding of the C^1 carbon suggests the following resonating structures (**IIIa–c**) [15].



(IIIa) (IIIb) (IIIc)

Table 1
Multinuclear NMR (^{1}H, ^{13}C, ^{199}Hg) data (δ (ppm), J (Hz)) of the ligand and mercury(II) compounds

^{1}H NMR [a]

Compound	$\delta[N^1H_2]$	$\delta[N^2H]$	$\delta[C^9H_3]$	$\delta[C^{4,8}H]$	$\delta[C^{5,6,7}H]$
Hatsc	8.31s, br 7.92s [d]	10.24s	2.29s	7.92m	7.38m
$HgCl_2(Hatsc\text{-}S)_2$	9.11s 8.79s	10.91s	2.41s	7.98m	7.41m

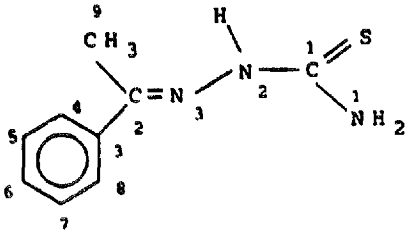
^{13}C NMR [a]

Compound	δC^1	δC^2	δC^9	δC^3	δC^6	$\delta C^{4,8}$	$\delta C^{5,7}$
Hatsc	179.1	148.0	14.0	137.7	129.3	128.3	126.6
$HgCl_2(Hatsc\text{-}S)_2$	174.0	152.5	15.3	137.3	130.3	128.6	127.4

^{199}Hg NMR

Compound	$\delta(Hg)$ [c]	$^3J(Hg\text{–}H)$
$HgCl_2(Hatsc\text{-}S)_2$ [a]	−838s, br	
Ph_2Hg [b]	−748t	173

[a] Solvent, dmso-d_6.
[b] Solvent, $CDCl_3$.
[c] δ values relative to neat Me_2Hg.
[d] Phenyl proton incorporates.



The low-field shift of the $^{13}C^2$ signal reveals that structure **IIIb** makes a significant contribution to the resonating structure.

The ^{199}Hg NMR spectrum of complex **A** shows a signal at δ = −838s, and this position is different from that of PhHgCl (δHg, −1092 ppm) [3]. Tertiary phosphine complexes, $HgCl_2(PPh_3)_2$ and $Hg(O_2CCF_3)_2(PPh_3)_2$ have δHg of −413 and −893 ppm, respectively. It shows that shielding of ^{199}Hg in complex **A** is somewhat lower than that of the $Hg(O_2CCF_3)_2(PPh_3)_2$ complex but much higher than that of $HgCl_2(PPh_3)_2$. In comparison, δHg values for the phenylmercury(II) complexes (δHg, $PhHg(O_2CCF_3)(OPPh_3)$, −1246; $PhHg(O_2CCH_3)(SPPh_3)$, −1405, $PhHg(O_2CCCl_3)(SePPh_3)$, −1123) which do not show symmetrisation are all upfield relative to complexes which exhibit this phenomenon [3,16]. The solid **B** showed a ^{199}Hg NMR signal at δ −749t (t, triplet) with ^3J(Hg–H) coupling constant of 173 Hz, and this confirms the formation of Ph_2Hg and $HgCl_2(Hatsc)_2$ as the products of the symmetrisation reaction [17].

Based on the above data, a tetrahedral structure for $HgCl_2(Hatsc)_2$ is suggested in which Hatsc is coordinating to Hg(II) via its thione sulfur. The X-ray crystallography on analogous complexes, $MX_2(HL)_2$ (M, X, HL: Co, I, Hatsc; Ni, Cl, Hatsc; Hg, Cl, Br, thiosemicarbazide) [9,18] have established their tetrahedral structures coordinating via thione sulfur only.

Acknowledgements

Professor T.S. Lobana thanks Dirección General de Investigación Científica y Técnica del Ministerio de Educación y Ciencia (SAB 95-0185), Spain for financial support and the Guru Nanak Dev University, Amritsar, Punjab, India for sanctioning leave.

References

[1] (a) J.L. Wardell, in G. Wilkinson (ed.), Comprehensive Organometallic Chemistry, Vol. 2, Pergamon, Oxford, 1982, p. 863; (b) R. Jensen and B. Rickborn, Electrophilic Substitution of Organomercurials, McGraw-Hill, New York, 1968, Ch. 6; (c) T.S. Lobana, Coord. Chem. Rev., 63 (1985) 161.
[2] T.S. Lobana, M.K. Sandhu, D.C. Povey and G.W. Smith, J. Chem. Soc., Dalton Trans., (1988) 2913.
[3] T.S. Lobana and M.K. Sandhu, Indian J. Chem., Sect. A, 29 (1990) 394.
[4] T.S. Lobana, M.K. Sandhu, D.C. Povey, G.W. Smith and V. Ramdas, J. Chem. Soc., Dalton Trans., (1989) 2339.

[5] (a) P.L. Barbaro, F. Cecconi, C.A. Ghilardi, S. Midollini, A. Orlandini and A. Vacca, Inorg. Chem., 33 (1994) 6163; (b) F. Cecconi, C.A. Ghilardi, S. Midollini, A. Orlandini and A. Vacca, J. Organomet. Chem., 510 (1996) 153.

[6] (a) D.X. West, S.B. Padhye and P.B. Sonawane, Struct. Bonding (Berlin), 76 (1991) 1; (b) M.J.M. Campbell, Coord. Chem. Rev., 15 (1975) 279; (c) S.B. Pandhye and G.B. Kauffman, Coord. Chem. Rev., 63 (1985) 127; (d) D.X. West, A.E. Liberta, S.B. Padhye, R.C. Chikate, P.B. Sonawane, A.S. Kumbhar and R.G. Yerande, Coord. Chem. Rev., 123 (1993) 49; (e) S.E. Livingstone, Q. Rev. Chem. Soc. 19 (1965) 386; (f) M. Akbar Ali and S.E. Livingstone, Coord. Chem. Rev., 13 (1974) 101.

[7] (a) C.E. Holloway and M. Melnik, Main Group Met. Chem., 17 (1994) 799 (review); (b) J. Organomet. Chem., 495 (1995) 1 (review).

[8] (a) K.M. Thimmaiah, G.T. Chandrappa, Rangaswamy and Jayarama, Polyhedron, 3 (1984) 1237; (b) H.K. Parvana and G. Singh, Indian J. Chem., 26A (1987) 581; (c) K.K. Aravindakshan and C.G.R. Nair, Indian J. Chem., 20A (1981) 684.

[9] (a) C. Chieh, Can. J. Chem., 55 (1977) 1583; (b) C. Chieh, L.P.C. Lee and C. Chiu, Can. J. Chem., 56 (1978) 2526.

[10] J. Zukerman-Schpector, M.C. Rodríguez-Argüelles, M.I. Suárez, A. Sánchez, J.S. Casas and J. Sordo, J. Coord. Chem., 24 (1991) 177.

[11] A. Macías, M.C. Rodríguez-Argüelles, M.I. Suárez, A. Sánchez, J.S Casas, J. Sordo and U. Englert, J. Chem. Soc., Dalton Trans., (1989) 1787.

[12] (a) S. Puniyani and T.S. Srivastava, Indian J. Chem. Sect A, 24 (1985) 240; (b) J.S. Casas, A. Sánchez, J. Sordo, A. Vázquez-López, E.E Castellano, J. Zukerman- Schpector, M.C. Rodriguez-Argüelles anc U. Russo, Inorg. Chim. Acta, 216 (1994) 169; (c) J.S. Casas, A Castiñeiras, A. Sánchez, J. Sordo, A. Vázquez-López, M.C Rodriguez-Argüelles and U. Russo, Inorg. Chim. Acta, 221 (1994) 61.

[13] G.E. Coates and D. Ridley, J. Chem. Soc., (1964) 166.

[14] (a) J.S. Casas, M.V. Castaño, M.S. García-Tasende, I. Martínez-Santamaría, A. Sánchez, J. Sordo, E.E. Castellano and J. Zukerman-Schpector, J. Chem. Res., (1992) 324; (b) J.S. Casas, M.V. Castaño, M.C. Rodríguez-Argüelles, A. Sánchez and J. Sordo, J. Chem. Soc., Dalton Trans., (1993) 1253.

[15] A.M. Brodie, H.D. Holden, J. Lewis and M.J. Taylor, J. Chem. Soc., Dalton Trans., (1986) 633.

[16] R.J. Goodfellow, in J. Mason (ed.), Multinuclear NMR, Plenum, New York, 1987, p. 563.

[17] P.A.W. Dean, Can. J. Chem., 57 (1979) 754.

[18] (a) C. Bellitto, A.A.G. Tomlinson, C. Furlani and G. De Munno, Inorg. Chim. Acta, 21 (1978) 269; (b) P. Dapporto, G. De Munno and A.A.G. Tomlinson, J. Chem. Res., 40 (1984) 501.