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SHORT PAPER

Complexes of diorganotin(IV) dihalides with *N,N'*-dimethyl-2,2'-bisimidazole

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Adducts of *N,N'*-dimethyl-2,2'-bisimidazole (DMBIm) with diethyl- and dibutyl-tin(IV) dihalides (Cl, Br) have been isolated and characterized. IR data for [SnR_2X_2(DMBIm)] compounds are in keeping with a six-coordinate tin atom with DMBIm acting as a bidentate ligand, whereas in [$(SnR_2X_2)_2$(DMBIm)] the tin is five-coordinate and DMBIm acts as a bridging ligand. Measurements of conductivity in acetonitrile show the adducts to behave as non-ionogens in this solvent. NMR data show them to undergo dissociation in $CDCl_3$.

Keywords: *N,N'*-Dimethyl-2,2'-bisimidazole, diorganotin(IV) dihalides, complexes

INTRODUCTION

Being interested in the preparation of complexes of dialkyltin(IV) dihalides with bidentate ligands coordinating via nitrogen, some of which show antitumour activity,[1,2] in previous work we studied the reaction of SnR_2X_2 with the ligand 2,2'-bisimidazole (H_2BIm), obtaining complexes of the type [$(SnR_2X_2)_n$(H_2BIm)] ($n=1$, 2; R = Me, Et, Bu).[3] Solubility problems arising in preliminary assays of their inhibitory effects on tumour cell division were attributed to the low solubility of the ligand. We therefore prepared the more soluble ligand *N,N'*-dimethyl-2,2'-bisimidazole (DMBIm), and studied its interaction with the SnR_2X_2 halides. In a previous paper[4] we describe the reaction of DMBIm with $SnMe_2X_2$ (X = Cl, Br); we now report the results obtained with $SnEt_2X_2$ and $SnBu_2X_2$, which afforded compounds of the type [$(SnR_2X_2)_2$(DMBIm)] and [SnR_2X_2(DMBIm)] (X = Cl, Br). Pending completion of the structural characterization and biological assays of these compounds, in this communication we describe their synthesis and some structural characteristics.

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EXPERIMENTAL

Reagents

Diethyltin dichloride, diethyltin dibromide, dibutyltin dichloride and dibutyltin dibromide (Ventron) were used as supplied. Solvents were purified by the usual methods. DMBIm was prepared as described in the literature.[5,6]

Preparation of compounds

[$SnEt_2Cl_2$(DMBIm)]
A solution of $SnEt_2Cl_2$ (0.91 mmol) in CH_2Cl_2 (*ca* 15 ml) was added dropwise to a solution of DMBIm (0.91 mmol) in CH_2Cl_2 (*ca* 15 ml). The mixture was stirred, the solvent was partially evaporated, and the solid formed upon cooling was filtered off and dried *in vacuo*.

[$SnEt_2Br_2$(DMBIm)]
This was prepared similarly using 0.71 mmol each of $SnEt_2Br_2$ and DMBIm.

[$(SnEt_2Cl_2)_2$(DMBIm)]
A solution of $SnEt_2Cl_2$ (4.8 mmol) in CH_2Cl_2 (*ca* 15 ml) was added dropwise to a solution of DMBIm (2.4 mmol) in CH_2Cl_2 (*ca* 15 ml). The mixture was stirred, the solvent was partially evaporated and the solid formed was filtered off and dried *in vacuo*.

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Table 1. Analytical data, colours, melting points and molar conductivities of the compounds prepared

Compound	Analysis (%)[a] C	N	H	Colour	M.pt (°C)	Λ_M ($S\,cm^2\,mol^{-1}$)
DMBIm	58.2 (59.2)	33.9 (34.5)	6.0 (6.2)	Beige	113	—
$[SnEt_2Cl_2(DMBIm)]$	34.5 (35.2)	13.2 (13.7)	4.2 (4.9)	Beige	63	23.3
$[SnEt_2Br_2(DMBIm)]$	28.8 (28.9)	11.2 (11.2)	4.0 (4.0)	White	150	17.5
$[(SnEt_2Cl_2)_2(DMBIm)]$	28.7 (29.2)	8.9 (8.5)	5.9 (4.6)	Beige	70	55.9
$[(SnEt_2Br_2)_2(DMBIm)]$	23.1 (23.0)	7.2 (6.7)	4.6 (3.6)	White	111	22.7
$[SnBu_2Cl_2(DMBIm)]$	40.7 (41.2)	11.1 (12.0)	6.1 (6.1)	White	93	12.5
$[SnBu_2Br_2(DMBIm)]$	34.1 (34.6)	9.5 (10.1)	6.1 (5.1)	White	118	13.3
$[(SnBu_2Cl_2)_2(DMBIm)]$	37.1 (37.4)	8.6 (7.3)	7.2 (6.0)	Yellow	65	—
$[(SnBu_2Br_2)_2(DMBIM)]$	30.1 (30.4)	5.4 (5.9)	5.9 (4.9)	Yellow	63	83.4

[a] The theoretical percentages are given in parentheses.

$[(SnEt_2Br_2)_2(DMBIm)]$
This was prepared similarly using 2.6 mmol of $SnEt_2Br_2$ and 1.3 mmol of DMBIm.

$[SnBu_2Cl_2(DMBIm)]$
A solution of DMBIm (0.51 mmol) in CH_2Cl_2 (*ca* 20 ml) was added dropwise to a solution of $SnBu_2Cl_2$ (0.51 mmol) in CH_2Cl_2 (*ca* 20 ml). After being stirred, the solvent was partially evaporated and the solid formed was filtered off and dried *in vacuo*.

$[SnBu_2Br_2(DMBIm)]$
This was prepared similarly using 0.52 mmol each of $SnBu_2Br_2$ and DMBIm.

$[(SnBu_2Cl_2)_2(DMBIm)]$
A solution of $SnBu_2Cl_2$ (1.0 mmol) in CH_2Cl_2 (*ca* 20 ml) was added dropwise to a solution of DMBIm (0.51 mmol) in CH_2Cl_2 (*ca* 20 ml). After being stirred, the solvent was partially evaporated and the solid formed was filtered off and dried *in vacuo*.

$[(SnBu_2Br_2)_2(DMBIm)]$
This was prepared similarly using 0.59 mmol of DMBIm and 0.30 mmol of $SnBu_2Br_2$.

Chemical analysis

C, H and N were determined using a Carlo Erba 1108 microanalyser. The results are listed in Table 1, which also shows colours, melting points and conductivities.

Physical measurements

Melting points were determined in a Büchi apparatus. IR spectra (4000–200 cm^{-1}) were recorded in Nujol mulls or KBr discs with a Perkin–Elmer 1330 spectrophotometer. Molar conductivities (10^{-3} M in acetonitrile) were measured with a WTW LF-3 conductivity meter. ^{1}H (250.13 MHz) and ^{119}Sn (93.276 MHz) NMR spectra were recorded in $CDCl_3$ at room temperature on a Bruker WM-250 spectrometer and were referred to the solvent signal (7.27) and external neat $SnMe_4$, respectively.

RESULTS AND DISCUSSION

The reactions of SnR_2X_2 with DMBIm give 1 : 1 or 2 : 1 adducts depending on the mole ratio of the reagents. These products are solids with low melting points, are stable to light and in dry air, but are hydrolysed (especially the 2:1 adducts) by moisture. They are soluble in polar organic solvents, but only very poorly soluble in non-polar solvents.

IR spectra

The small frequency shifts induced by coordination in the most significant ring stretching vibrations of the ligand (1600–1300 cm^{-1}) are similar to those previously detected in the complexes with $SnMe_2X_2$ halides[4] and to those reported for imidazole[7] and 2,2'-bisimidazole complexes.[3] These shifts are in keeping with bonding through the pyridine-like nitrogen and with the small structural modifications in the imidazole rings found in the related system $[SnMe_2Br_2(DMBIm)]$.[4]

Table 2 lists selected infrared data in the 600–200 cm^{-1} range. The positions of the ν(Sn–C) bands of the $[(SnR_2X_2)_2(DMBIm)]$ complexes are close to their positions in the spectra of the $[SnR_2X_2(DMBIm)]$ complexes, as was found previously for the dimethyldihalotin(IV) complexes of this ligand[4] and for the complexes of the related ligand 2,2'-bisimidazole.[3] As found for the latter compounds, the intensity of ν_{sym}(Sn–C) is greater in the 2:1 than in the 1:1 complexes, which may indicate the presence of an angular C–Sn–C fragment.[3,8] The Sn–Cl stretching vibrations of both the 1:1 and 2:1 compounds have positions close to those found for the complexes of the related ligand 2,2'-bisimidazole with the same acceptor.[3] As in this latter case and in that of $[(SnMe_2X_2)_n(DMBIm)]$,[4] these bands lie at higher wavenumbers for the 2:1 than for the 1:1 complexes. This is in keeping[9] with the coordination number being smaller in the former (five) than in the latter (six),[3,4,10,11] the ligand acting as a bridge in the 2:1 complexes and as a chelating ligand in the 1:1 complexes.[4] As was observed previously for this ligand[4] and for 2,2'-bisimidazole complexes,[3] the IR spectra of the 2:1 and 1:1 compounds differ slightly as regards the ligand bands, but these differences do not allow chelating and bridging functions to be distinguished.[12]

Solution studies

The solubility of the complexes in acetonitrile was sufficient for measurement of their conductivities (Table 1). Although the molar conductivity values are in all cases lower than those for 1:1 electrolytes in acetonitrile (120–160 S cm^2 mol^{-1}),[13] in general they are higher for 2:1 complexes, probably because of solvolytic processes in these systems.

Previous studies of organotin(IV) dihalide complexes with ligands coordinating via nitrogens[3,4,14] have found the ligand to be dissociated in $CDCl_3$ solution. In this work we investigated this possibility for the complexes $[SnEt_2Cl_2(DMBIm)]$ and $[(SnEt_2Cl_2)_2(DMBIm)]$. Table 3 shows the ^1H NMR data for these complexes in $CDCl_3$. The ligand signals are virtually unshifted with respect to those of uncomplexed DMBIm, suggesting extensive dissociation and exchange in solution. The values of $^2J(^{117/119}Sn-^1H)$, which is very sensitive to the coordination number of tin, are also indicative of weak donor–acceptor interaction because they are close to the value for the free acceptor in $CDCl_3$. The dissociation was confirmed by ^{119}Sn

Table 2. Assignments of the main IR bands[a] of the complexes (600–200 cm^{-1})

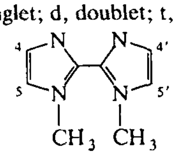
Compound	ν_{asym}(Sn–C)	ν_{sym}(Sn–C)	ν(Sn–X)
$[SnEt_2Cl_2(DMBIm)]$	540 m	500 w	240 m
$[SnEt_2Br_2(DMBIm)]$	525 m	—	—
$[(SnEt_2Cl_2)_2(DMBIm)]$	560m, b	490 w	320 m 310 m
$[(SnEt_2Br_2)_2(DMBIm)]$	530 m	490 m	—
$[SnBu_2Cl_2(DMBIM)]$	600 m	520 w	240 m 220 m
$[SnBu_2Br_2(DMBIm)]$	595 m	520 w	—
$[(SnBu_2Cl_2)_2(DMBIm)]$	595 m	520 m	330 m 275 s, b
$[(SnBu_2Br_2)_2(DMBIm)]$	590 s	520 w	—

[a] Abbreviations: w, weak; m, medium; s, strong; b, broad.

Table 3. NMR parameters[a] (δ, ppm; J, Hz) for DMBIm, $SnEt_2Cl_2$ and their complexes

Compound	$\delta(CH_3)$	$\delta(CH_2)$	$J(CH_2\text{–}CH_3)$	$^2J(^{117/119}Sn\text{–}^1H)$	$^3J(^{117/119}Sn\text{–}^1H)$	δ(ligand)[b]	$\delta(^{119}Sn)$
DMBIm	—	—	—	—	—	4.03(CH_3–N, s) 6.95(H–5,5′, d) 7.11(H–4,4′, d)	—
$SnEt_2Cl_2$	1.45(t)	1.78(m)	7.8	≈48.8	129.2/135.1	—	126.2
[$SnEt_2Cl_2$(DMBIM)][c]	1.40(t)	1.76(m)	7.8	≈55.1	134.9/141.3	4.01(CH_3–N, s) 7.01(H–5,5′, d) 7.17(H–4,4′, d)	11.7
[$(SnEt_2Cl_2)_2$(DMBIm)][c]	1.43(t)	1.78(m)	7.9	≈53.1	133.9/140.2	4.02(CH_3–N, s) 7.06(H–5,5′, d) 7.23(H–4,4′, d)	25.4

[a] Abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet.
[b] Numbering scheme:



[c] As added to the solvent.

NMR spectroscopy: the chemical shift in no case corresponds to that of the free acceptor in the same solvent, showing incomplete dissociation into the starting reagents; the increase in coordination number due to adduct formation produces an upfield shift in $\delta(^{119}Sn)$ that is very much smaller than would be expected for a coordination number change from four to six.[15]

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REFERENCES

1. Crowe, A J, Smith, P J and Atassi, G *Inorg. Chim. Acta*, 1984, 93: 179
2. Saxena, A K and Huber, F *Coord. Chem. Rev.*, 1989, 95: 109
3. Sánchez Gonzalez, A, Casas, J S, Sordo, J, Russo, U, Lareo, M I and Regueiro, B J *J. Inorg. Biochem.*, 1990, 39: 227
4. López, C, Sánchez Gonzalez, A, Garcia, M E, Casas, J S, Sordo, J, Graziani, R and Casellato, U *J. Organomet. Chem.*, 1992, 434: 261
5. Abushamleh, A and Goodwin, H *Aust. J. Chem.*, 1979, 32: 513
6. Melloni, P, Dradi, E and Logemann, W *J. Med. Chem.*, 1972, 15: 9
7. Alberte, B, Sánchez Gonzalez, A, García, E, Casas, J S, Sordo, J and Castellano, E E *J. Organomet. Chem.*, 1988, 338: 187
8. Rivarola, E, Camalli, M and Caruso, F *Inorg. Chim. Acta*, 1987, 126: 1
9. Adams, D M *Metal–Ligand and Related Vibrations*, Edward Arnold, London, 1967
10. Clark, R J H, Davies, A G and Puddephatt, R J *J. Chem. Soc.*, 1968, 1828
11. Clark, J P and Wilkins, C J *J. Chem. Soc.*, 1966, 871
12. Kirchner, C and Krebs, B *Inorg. Chem.*, 1987, 26: 3569
13. Geary, W J *Coord. Chem. Rev.*, 1971, 7: 81
14. Sánchez González, A, Alberte, B, Casas, J S, Sordo, J, Castiñeiras, A, Hiller, W and Strähle, J *J. Organomet. Chem.*, 1988, 353: 169
15. Otera, J *J. Organomet. Chem.*, 1981, 221: 57