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Transition-metal Schiff-base complexes as ligands in tin chemistry Part 6. Reactions of diorganotin(IV) dinitrates with M(3MeO-sal1,3pn) [M = Ni, Co or Zn; $H_2$3MeO-sal1,3pn = *N,N'*-bis(3-methoxysalicylidene)-propane-1,3-diamine]

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Abstract

Reactions of diorganotin(IV) dinitrates with M(3MeO-sal1,3pn) · H_2O (M = Ni, Co or Zn; $H_2$3MeO-sal1,3pn = *N,N'*-bis(3-methoxysalicylidene)propane-1,3-diamine) leads to nitrate migration from tin to the transition metal or zinc and the formation of intimate ion-paired bimetallic 1/1 addition complexes. In each of these complexes the tin atom is located in the plane of the Schiff-base oxygens and is coordinated by all four. The complexes $[SnBz_2(NO_3)]$ · $[M(3MeO\text{-}sal1,3pn)(NO_3)]$(M = Co or Zn) are isomorphous and each contains tin in a pentagonal bipyramidal environment with the four Schiff-base oxygens and a nitrate oxygen defining the equatorial plane. In the case of $\{[SnMe_2] \cdot [Ni(3MeO\text{-}sal1,3pn)(NO_3)(H_2O)]\}NO_3$, the tin is six-coordinated, but there is an additional weak intermolecular Sn–O interaction involving an oxygen of a nitrate coordinated to nickel. The complex $\{[SnMe_2(H_2O)] \cdot [Co(3MeO\text{-}sal1,3pn)(NO_3)(H_2O)]\}NO_3$ contains tin in a pentagonal bipyramidal environment with the Schiff-base oxygens and a water oxygen defining the equatorial plane. The crystal structures of both dimethyltin complexes display extensive hydrogen bonding.

Keywords: Tin; Nickel; Cobalt; Zinc; Schiff bases; Crystal structure

1. Introduction

The divalent metal salicylaldimine complexes shown in Fig. 1 are a fascinating group of ligands which we have shown to display a number of chelating modes [1–8]. First, the disposition of the methoxy and phenolic oxygens is such as to strongly favour hydrogen bonding interactions with water, and this hydrogen bonded water may then form a donor bond to a Lewis acid such as dimethyltin(IV) dichloride or triphenyltin(IV) chloride [3–5]. This type of behaviour is most commonly encountered when the imine nitrogen bridging group is a two-carbon-atom bridge. Secondly, a metal can be located within the plane of the phenolic and methoxy oxygens, where it is held by donor bonds from these atoms [1,6]. Thirdly, the metal salicylaldimine can act as a tridentate ligand (maintaining a free methoxy oxygen) so that two such ligands can complete octahedral geometry about a metal ion. This type of chelating behaviour is found in $Zn[Zn(3\text{-}MeOsal1,3pn)(NCS)]_2$ [7]. Fourthly, a metal ion may be sandwiched between two sets of salicylaldimine oxygens with all four oxygens of each salicylaldimine coordinating to the metal ion, an example of this behaviour is found in the complex structure of the 3 : 4 addition compound formed between $PbCl_2$ and Zn(3-MeOsal1,3pn) [8]. Finally, the metal salicylaldimine may function as a bidentate ligand to each of two metals of a bimetallic species, such as the two nickel atoms of the bimetallic ion $Ni_2(\mu\text{-}OH)2^{2+}$ [2].

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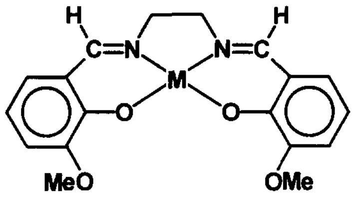

M(3MeO-sal1,3pn)
M = Co, Ni, Cu or Zn

Fig. 1. Ligands and nomenclature.

In a previous paper of this series [6] it was shown that when dialkyltin thiocyanates react with copper, nickel and zinc methoxysalicylaldimine complexes, the tin atom is located in the plane of the Schiff-base oxygens, where it is held by donor bonds from these atoms. In some instances both thiocyanates migrate to nickel thus leaving tin with a coordination number of six, while in other cases only one thiocyanate migrates to nickel, leaving tin with a coordination number of seven. In view of this behaviour, the question arises as to what would occur if the reacting diorganotin species contained bidentate ligands, such as nitrate, rather than thiocyanate ligands. Should a nitrate group maintain a bidentate chelating role at tin, tin could potentially become eight coordinate, a rarely encountered coordination number for a diorganotin(IV) species. However, if a nitrate group adopted a *cis* chelating role at nickel this would alter the usual planar arrangement of Schiff-base nitrogen and oxygen atoms and thus potentially result in a new chelating role for the metal salicylaldimine. In order to investigate these possibilities, a study of the reactions of diorganotin(IV) dinitrates with the metal salicylaldimines M(3MeO-sal1,3pn) · H_2O(M = Co, Ni or Zn; $H_2$3MeO-sal1,3pn = *N*,*N*′-bis(3-methoxysalicylidene)-1,3-diaminopropane) was undertaken.

2. Experimental details

2.1. Preparation and crystallisation of the complexes

The tin–zinc and the tin–cobalt complexes and $[SnMe_2L]$ · $[Ni(3MeO\text{-}sal1,3pn)(NO_3)L](NO_3)\}$ · H_2O (L = acetone) were prepared as follows. A mixture of dialkyltin dichloride (0.01 mol) and silver nitrate (0.02 mol) in dry acetone (approx. 150 cm^3) was refluxed under dinitrogen for 3 h, after which the silver chloride was filtered off under dinitrogen. The metal salicylaldimine (0.01 mol) was added as a solid to the acetone solution of the diorganotin dinitrate and refluxing was continued for approximately 4 h. The solid products were isolated by filtration and dried under vacuum. As a result of their considerable solubility in acetone, the cobalt complexes were isolated in only poor yield by this procedure. However, reduction of the filtrate volume under reduced pressure greatly enhanced the yields of solid products.

The preparation of $\{[SnMe_2]$ · $[Ni(3MeO\text{-}sal1,3pn)(H_2O)(NO_3)]\}(NO_3)$ was carried out in similar fashion, except that following the preparation of $SnMe_2(NO_3)_2$ and the removal of silver chloride the acetone solution of the organotin nitrate was evaporated to dryness and

Table 1
Analytical data (%) [a]

	C	N	H
$[SnBz_2(NO_3)]$ · $[Zn(3MeO\text{-}sal1,3pn)(NO_3)]$	47.85 (47.71)	7.00 (6.75)	4.16 (4.10)
$[SnBz_2(NO_3)]$ · $[Co(3MeO\text{-}sal1,3pn)(NO_3)]$	47.42 (47.97)	6.25 (6.78)	4.38 (4.16)
$\{[SnMe_2]$ · $[Ni(3MeO\text{-}sal1,3pn)(NO_3)(H_2O)]\}(NO_3)$	36.33 (36.56)	8.30 (8.12)	3.97 (4.09)
$\{[SnMe_2L]$ · $[Ni(3MeO\text{-}sal1,3pn)(NO_3)L](NO_3)\}$ · H_2O [b]	40.02 (40.23)	5.40 (6.95)	4.31 (4.97)
$\{[SnMe_2(H_2O)]$ · $[Co(3MeO\text{-}sal1,3pn)(NO_3)(H_2O)]\}(NO_3)$	36.10 (35.62)	7.76 (7.91)	4.20 (4.27)
$[SnPh_2(NO_3)]$ · $[Co(3MeO\text{-}sal1,3pn)(NO_3)]$	46.31 (46.64)	6.69 (7.02)	4.23 (4.26)

[a] Theoretical data in parentheses.
[b] L = acetone.

Table 2
Sn-119 Mössbauer [a], selected IR spectroscopic and magnetic data

	Δ (mm s^{-1})	δ (mm s^{-1})	ν(C=O) [b]	μ (BM)
$[SnBz_2(NO_3)]$ · $[Zn(3MeO\text{-}sal1,3pn)(NO_3)]$	4.24	1.60	1568	dia.
$[SnBz_2(NO_3)]$ · $[Co(3MeO\text{-}sal1,3pn)(NO_3)]$	4.09	1.54	1566	4.95
$\{[SnMe_2]$ · $[Ni(3MeO\text{-}sal1,3pn)(NO_3)(H_2O)]\}(NO_3)$	3.93	1.88	1571	3.00
$\{[SnMe_2L]$ · $[Ni(3MeO\text{-}sal1,3pn)(NO_3)L](NO_3)\}$ · H_2O [c]	4.59	1.46		2.95
$\{[SnMe_2(H_2O)]$ · $[Co(3MeO\text{-}sal1,3pn)(NO_3)(H_2O)]\}(NO_3)$	4.54	1.33	1564	4.24
$[SnPh_2(NO_3)]$ · $[Co(3MeO\text{-}sal1,3pn)(NO_3)]$	3.71	1.21	1564	4.91

[a] Parameters ±0.03 mm s^{-1}.
[b] ν(C=O) stretching frequencies for Zn(3MeO-sal1,3pn) · H_2O and its cobalt and nickel analogs are at 1548, 1544 and 1545 cm^{-1}, respectively.
[c] L = acetone.

30 cm^3 dry acetonitrile were added. The nickel salicylaldimine was added to the acetonitrile solution of the organotin nitrate, whereupon the product separated almost immediately as a pale blue powder.

Crystals of the cobalt complexes were grown from acetone while the best quality crystals of the zinc and nickel complexes were obtained from acetonitrile.

Analytical data for all complexes are given in Table 1.

2.2. X-ray crystallography

Crystallographic details are given in Table 3. All four structures were solved by direct methods, SHELX 86 [9], and refined by full-matrix least-squares, SHELXL-93 [10]. Data were corrected for Lorentz and polarisation effects but not for absorption. Hydrogen atoms were included in calculated positions for final refinement cycles. All non hydrogen atoms were refined anisotropically. Calculations were carried out on a VAX 6610 computer. Final atomic coordinates are in Tables 4–7. The programs ORTEP [11] and ORTEX [12] were used to produce the drawings of Figs. 2–4 and 6, and Figs. 5 and 7, respectively.

H-atom coordinates, thermal parameters and complete lists of bond lengths and angles, have been deposited at the Cambridge Crystallographic Data Centre.

3. Results and discussion

The nitrates $SnMe_2(NO_3)_2$, $SnBz_2(NO_3)_2$ and $SnPh_2(NO_3)_2$ reacted readily with the metal methoxysalicylaldimine complexes to yield the 1/1 addition complexes listed in Table 1. These are air-stable complexes, which are reasonably soluble in acetone, acetonitrile and THF, with the cobalt complexes the most soluble. It is clear from the colours of solutions of these addition complexes (compared with those of solutions of the parent metal Schiff-base comlexes) that dissocia-

Table 3
Crystallographic data

	A	B	C	D
Empirical formula	$C_{33}H_{34}N_4O_{10}SnZn$	$C_{33}H_{34}N_4O_{10}SnCo$	$C_{21}H_{26}N_4O_{11}SnNi$	$C_{21}H_{28}N_4O_{12}SnCo$
Formula weight	830.70	824.26	687.86	706.08
Temperature (K)	293(2)	293(2)	293(2)	293(2)
Wavelength (Å)	0.71069	0.71069	0.71069	0.71069
Crystal system	monoclinic	monoclinic	orthorhombic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_12_12_1$	$P2_1/c$
Unit cell dimensions (Å)	$a = 17.9999(13)$ $b = 10.5714(8)$ $c = 18.0998(14)$ $\alpha = 90.0°$ $\beta = 107.306(6)°$ $\gamma = 90.0°$	$a = 18.016(3)$ $b = 10.548(2)$ $c = 18.099(2)$ $\alpha = 90.0°$ $\beta = 107.413(10)°$ $\gamma = 90.0°$	$a = 10.052(2)$ $b = 13.404(2)$ $c = 18.761(3)$ $\alpha = 90.0°$ $\beta = 90.0°$ $\gamma = 90.0°$	$a = 9.633(2)$ $b = 13.874(2)$ $c = 20.482(3)$ $\alpha = 90.0°$ $\beta = 99.84(1)°$ $\gamma = 90.0°$
Volume ($Å^3$)	3288.2(4)	3281.8(9)	2527.9	2697.0
Z	4	4	4	4
Density (calc.) ($mg\ m^{-3}$)	1.678	1.668	1.807	1.734
Abs. coefficient (mm^{-1})	1.554	1.331	1.800	1.609
$F(000)$	1680	1668	1384	1412
Crystal size (mm)	0.57 × 0.54 × 0.54	0.25 × 0.25 × 0.2	0.4 × 0.2 × 0.2	0.3 × 0.25 × 0.22
θ-range for data collection	2.26–31.97	2.26–25.92	2.17–23.96	2.02–23.97
Index ranges	$0 \leq h \leq 26$ $0 \leq k \leq 15$ $-26 \leq l \leq 25$	$0 \leq h \leq 20$ $0 \leq k \leq 12$ $-20 \leq l \leq 20$	$0 \leq h \leq 11$ $0 \leq k \leq 14$ $0 \leq l \leq 19$	$0 \leq h \leq 10$ $0 \leq k \leq 14$ $-21 \leq l \leq 21$
Reflections collected	12060	6727	2286	4483
Independent reflections	11378 [R(int) = 0.0189]	6304 [R(int) = 0.0145]	2218 [R(int) = 0.0062]	4122 [R(int) = 0.0172]
Refinement method	Full-matrix-least-squares on F^2	Full-matrix-least-squares on F^2	Full-matrix-least-squares on F^2	Full-matrix-least-squares on F^2
Data/restraints/param.	11378/0/442	6304/0/444	2218/0/343	4122/0/352
Goodness-of-fit on F^2	1.079	1.027	0.868	0.947
Final R indices ($I > 2\sigma I$) [a]	$R_1 = 0.034$ $wR_2 = 0.0936$	$R_1 = 0.030$ $wR_2 = 0.0764$	$R_1 = 0.0335$ $wR_2 = 0.0873$	$R_1 = 0.0349$ $wR_2 = 0.1099$
Final R indices (all data)	$R_1 = 0.0423$ $wR_2 = 0.0971$	$R_1 = 0.0581$ $wR_2 = 0.0821$	$R_1 = 0.0371$ $wR_2 = 0.0916$	$R_1 = 0.0504$ $wR_2 = 0.1189$
Largest difference peak and hole (e $Å^{-3}$)	0.720 and −1.188	0.980 and −0.466	1.529 and −0.750	1.184 to −0.451

[a] There were 9454, 4441, 2071 and 3212 reflections with $I > 2\sigma I$ for A, B, C and D respectively.

tion does not occur, to any appreciable extent in solution. The nickel complexes are paramagnetic and the cobalt complexes are high-spin complexes thus substantiating that neither of these metal ions are in square-planar environments; this observation is consistent with the migration of a nitrate group from tin to the transition metal. The phenolic ν(C–O) stretching vibration in the IR spectrum of each of the complexes is at a considerably higher frequency than that for the parent metal Schiff-base complex, and this is consistent with a strong interaction between tin and the phenolic oxygens such as occurs when tin lies in the plane of the phenolic and methoxy oxygens [6]. The location of tin, along with the migration of a nitrate group to the transition metal were verified by crystallographic studies on four of the complexes listed in Table 1.

Table 4
Atomic coordinates ($\times 10^4$) for **A**

	x	*y*	*z*
SN(1)	3649(1)	1198(1)	1148(1)
Zn(1)	1996(1)	−143(1)	−78(1)
O(1)	4550(1)	−646(2)	1527(1)
O(2)	3224(1)	3417(2)	1255(1)
O(3)	3166(1)	−508(1)	524(1)
O(4)	2476(1)	1575(1)	400(1)
O(5)	892(2)	−1764(3)	1286(1)
O(6)	1639(1)	−598(3)	849(1)
O(7)	759(2)	−1708(4)	87(2)
O(8)	5912(2)	1872(4)	1884(3)
O(9)	5386(3)	3661(3)	1708(2)
O(10)	4789(1)	2097(2)	2067(1)
N(1)	2052(1)	−1655(2)	−787(1)
N(2)	1156(1)	835(2)	−874(1)
N(3)	1099(1)	−1362(2)	758(1)
N(4)	5381(1)	2572(3)	1891(2)
C(1)	3593(1)	−1529(2)	491(1)
C(2)	4330(1)	−21658(2)	1039(1)
C(3)	4786(1)	−2721(2)	1058(2)
C(4)	4526(2)	−3654(2)	505(2)
C(5)	3827(2)	−3523(2)	−68(2)
C(6)	3341(1)	−2463(2)	−77(1)
C(7)	2613(2)	−2437(2)	−685(1)
C(8)	1357(2)	−1935(3)	−1441(2)
C(9)	990(2)	−785(3)	−1895(1)
C(10)	591(1)	98(3)	−14747(2)
C(11)	1053(1)	2037(2)	−901(1)
C(12)	1509(1)	2982(2)	−385(1)
C(13)	1243(1)	4241(2)	−522(2)
C(14)	1612(2)	5214(2)	−60(2)
C(15)	2281(2)	4980(2)	551(2)
C(16)	2556(1)	3760(2)	685(1)
C(17)	2180(1)	2731(2)	235(1)
C(18)	5183(1)	−829(3)	2221(1)
C(19)	3547(2)	4330(3)	1853(2)
C(20)	3308(1)	−1445(3)	2425(2)
C(21)	3588(2)	−2465(3)	2906(2)
C(22)	4119(2)	−2274(3)	3634(2)
(23)	4370(2)	−1089(3)	3858(2)
(24)	4099(1)	−61(2)	3375(1)
(25)	3562(1)	−227(2)	2646(1)
(26)	3259(1)	892(2)	2143(1)
(27)	3535(2)	686(3)	−960(1)
(28)	3021(2)	722(5)	−1700(2)
(29)	2647(2)	1822(6)	−1985(2)
(30)	2792(3)	2875(5)	−1553(2)
(31)	3311(2)	2871(3)	−809(2)
(32)	3680(1)	1763(2)	−500(1)
(33)	4215(1)	1722(3)	305(1)

Table 5
Atomic coordinates ($\times 10^4$) for **B**

	x	*y*	*z*
Sn(1)	3657(1)	1197(1)	1164(1)
Co(1)	2017(1)	−129(1)	−71(1)
O(1)	2479(1)	1569(2)	406(1)
O(2)	3173(1)	−523(2)	542(1)
O(3)	3227(1)	3418(2)	1259(2)
O(4)	4553(1)	−651(2)	1547(1)
O(5)	4790(2)	2097(3)	2080(2)
O(6)	5915(2)	1886(5)	1901(3)
O(7)	5373(3)	3664(4)	1719(3)
O(8)	1668(2)	−540(5)	896(2)
O(9)	897(2)	−1750(4)	1254(2)
O(10)	887(4)	−1616(5)	98(3)
N(1)	1155(2)	834(3)	−860(2)
N(2)	2074(2)	−1628(3)	−796(2)
N(3)	5384(2)	2572(4)	1906(2)
N(4)	1152(2)	−1299(3)	782(2)
C(1)	2178(2)	2737(3)	234(2)
C(2)	2557(2)	3761(3)	685(2)
C(3)	2287(2)	4982(3)	541(2)
C(4)	1624(2)	5215(4)	−66(2)
C(5)	1254(2)	4246(4)	−519(2)
C(6)	1514(2)	2984(3)	−384(2)
C(7)	1056(2)	2026(4)	−895(2)
C(8)	590(2)	84(4)	−1461(2)
C(9)	1000(3)	−780(4)	−1886(2)
C(10)	1374(3)	−1912(4)	−1447(2)
C(11)	2633(2)	−2418(4)	−687(2)
C(12)	3361(2)	−2458(3)	−76(2)
C(13)	3842(3)	−3512(3)	−65(3)
C(14)	4530(3)	−3648(4)	506(3)
C(15)	4792(2)	−2722(4)	1065(2)
C(16)	4337(2)	−1665(3)	1050(2)
C(17)	3600(2)	−1534(3)	500(2)
C(18)	3552(3)	4335(4)	1863(2)
C(19)	5190(2)	−835(4)	2242(2)
C(20)	3267(2)	895(4)	2157(2)
C(21)	3572(2)	−207(3)	2666(2)
C(22)	4103(2)	−47(4)	3395(2)
C(23)	4379(2)	−1064(4)	3879(2)
C(24)	4129(3)	−2264(4)	3653(3)
C(25)	3608(3)	−2450(4)	2941(3)
C(26)	3320(2)	−1437(4)	2445(2)
C(27)	4219(2)	1720(4)	316(2)
C(28)	3682(2)	1764(4)	−487(2)
C(29)	3317(3)	2875(5)	−796(3)
C(30)	2803(4)	2900(8)	−1530(4)
C(31)	2656(3)	1844(10)	−1970(3)
C(32)	3021(3)	732(7)	−1689(3)
C(33)	3534(3)	698(4)	−950(2)

The asymmetric units of the 1/1 addition complexes formed between dibenzyltin dinitrate and M(3MeO-sal1,3pn) · H_2O[M = Zn (**A**) or Co (**B**)] and the 1/1

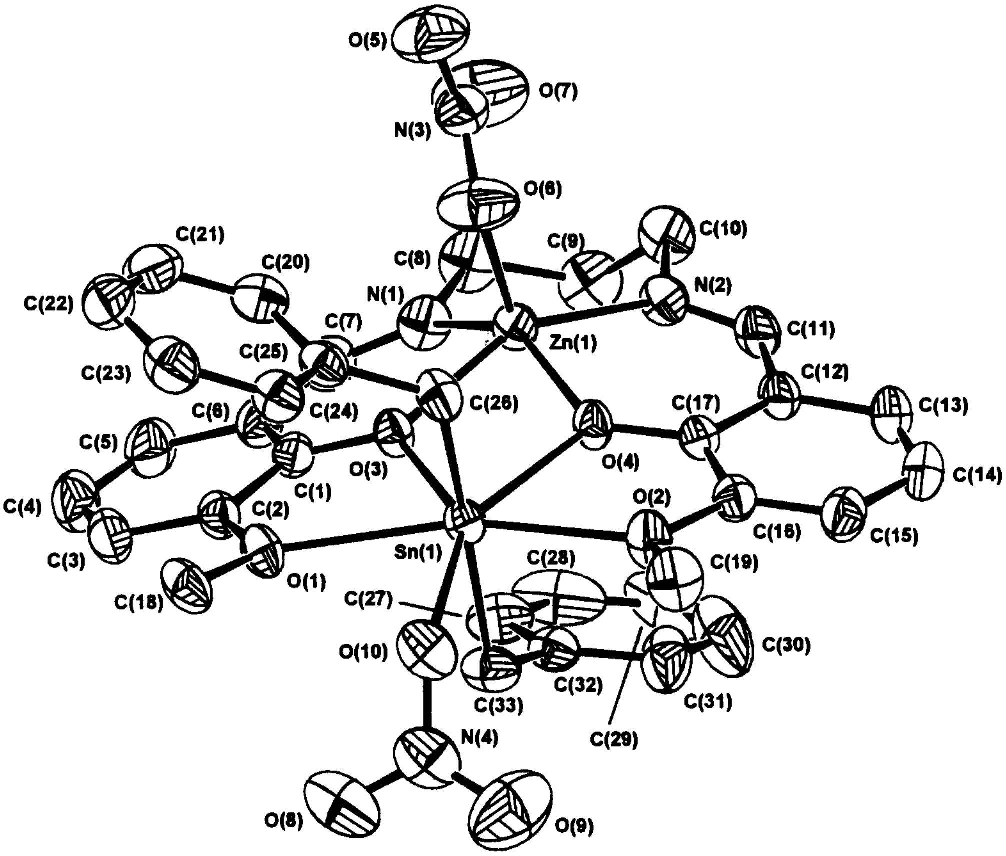

Fig. 2. The asymmetric unit of **A**.

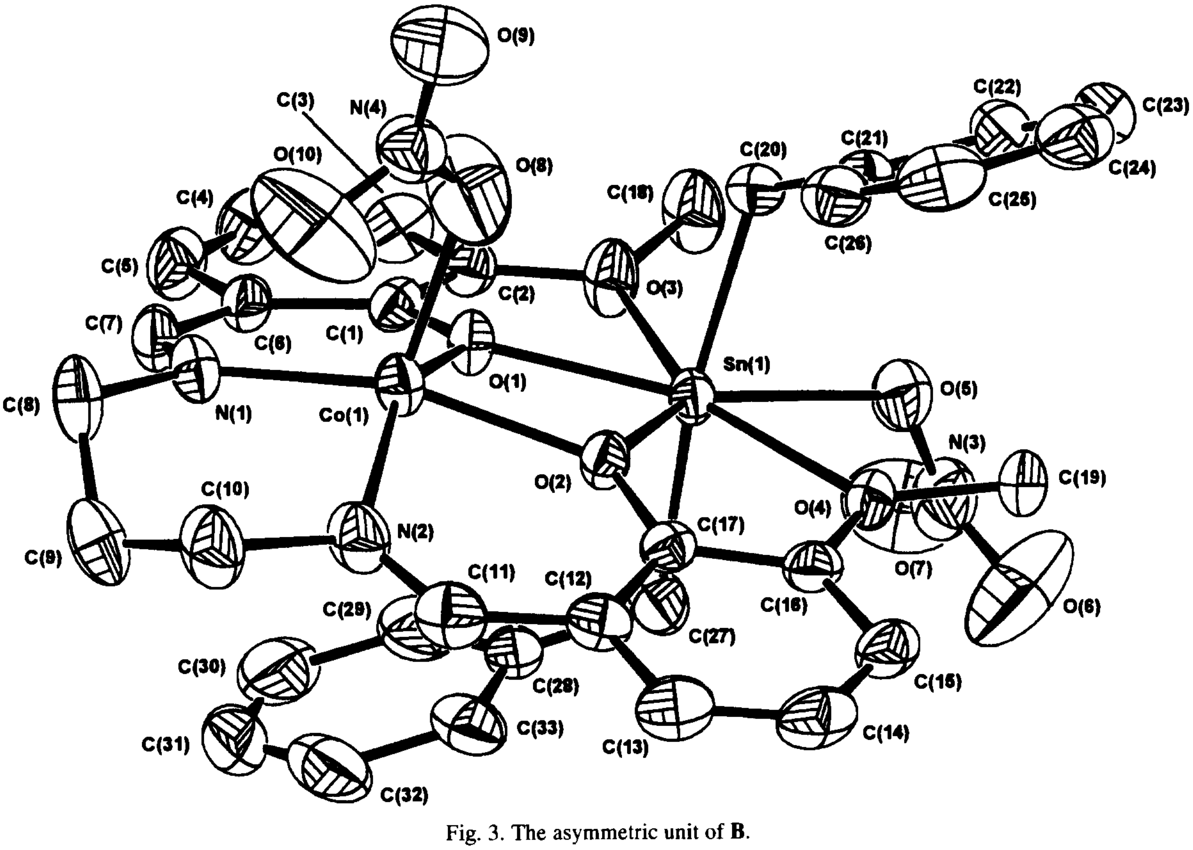

Fig. 3. The asymmetric unit of **B**.

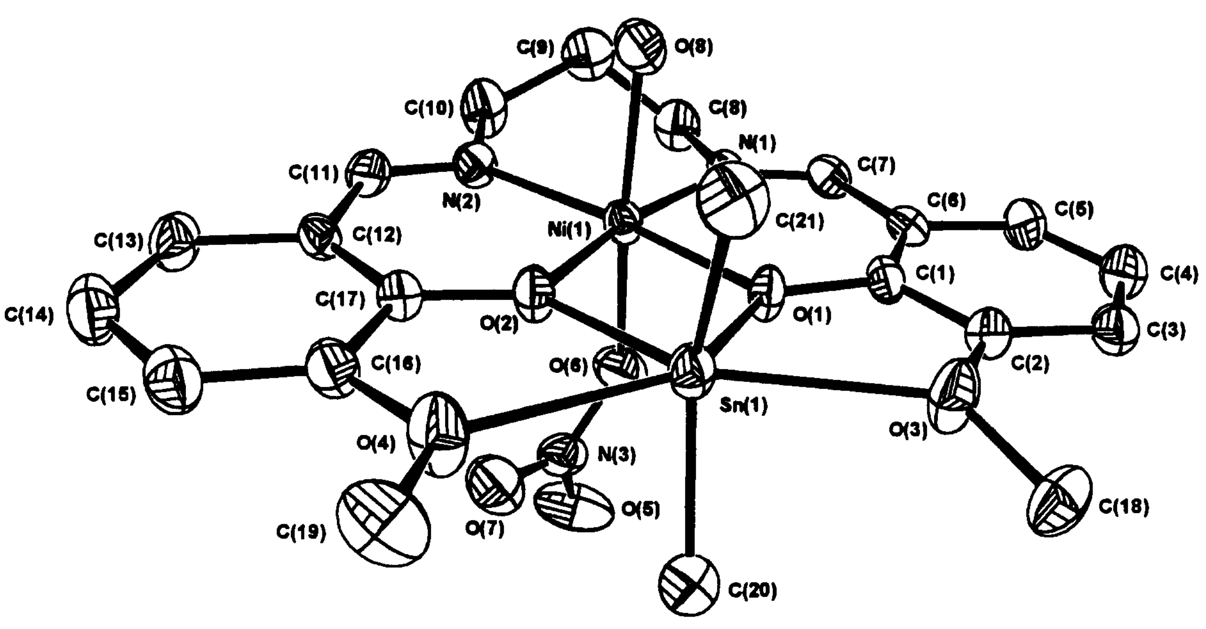

Fig. 4. The asymmetric unit of **C** (the uncoordinated nitrate ion is omitted).

Table 6
Atomic coordinates ($\times 10^4$) for **C**

	x	*y*	*z*
Sn(1)	608(1)	9039(1)	7991(1)
Ni(1)	−819(1)	9872(1)	9442(1)
O(1)	913(4)	9965(3)	8874(2)
O(2)	−1179(4)	9046(3)	8562(2)
O(3)	2932(5)	9723(4)	8026(3)
O(4)	−1200(5)	8107(4)	7352(3)
O(5)	−2493(9)	12426(5)	8459(3)
O(6)	−1447(6)	11306(4)	9053(3)
O(7)	−2589(7)	10908(5)	8116(3)
O(8)	−119(5)	8570(4)	9925(3)
O(9)	820(5)	1713(5)	5748(3)
O(10)	2353(8)	1783(5)	4974(3)
O(11)	2660(7)	907(5)	5899(3)
N(2)	−2628(5)	9559(4)	9846(3)
N(3)	−2191(7)	11546(5)	8534(3)
N(4)	1942(6)	1458(4)	5545(3)
C(1)	2094(6)	10361(4)	9087(3)
C(2)	3177(6)	10289(5)	8638(4)
C(3)	4385(7)	10705(5)	8786(4)
C(4)	4503(8)	11258(6)	9426(4)
C(5)	3459(7)	11327(6)	9879(4)
C(6)	2201(6)	10886(5)	9722(3)
C(7)	1178(7)	11011(5)	10249(4)
C(8)	−895(8)	10941(5)	10822(4)
C(9)	−1779(8)	10106(7)	11030(4)
C(10)	−2979(7)	9931(7)	10554(4)
C(11)	−3494(6)	9006(5)	9540(4)
C(12)	−3425(6)	8553(5)	8845(3)
C(13)	−4563(7)	8025(5)	8620(4)
C(14)	−4610(7)	7543(5)	7971(4)
C(15)	−3480(7)	7562(5)	7524(4)
C(16)	−2366(7)	8052(5)	7738(4)
C(17)	−2312(7)	8561(5)	8390(3)
C(18)	3839(7)	9763(6)	7431(4)
C(19)	−1063(9)	7541(6)	6719(4)
C(20)	334(8)	10010(6)	7123(4)
C(21)	1491(8)	7667(5)	8264(4)

addition complexes formed between dimethyltin dinitrate and M(3MeO-sal1,3pn) · H_2O(M = Ni(**C**) or Co (**D**)) are shown in Figs. 2–4 and 6. The complexes share two structural features, the position of the tin atom and the monodentate coordination of a nitrate to

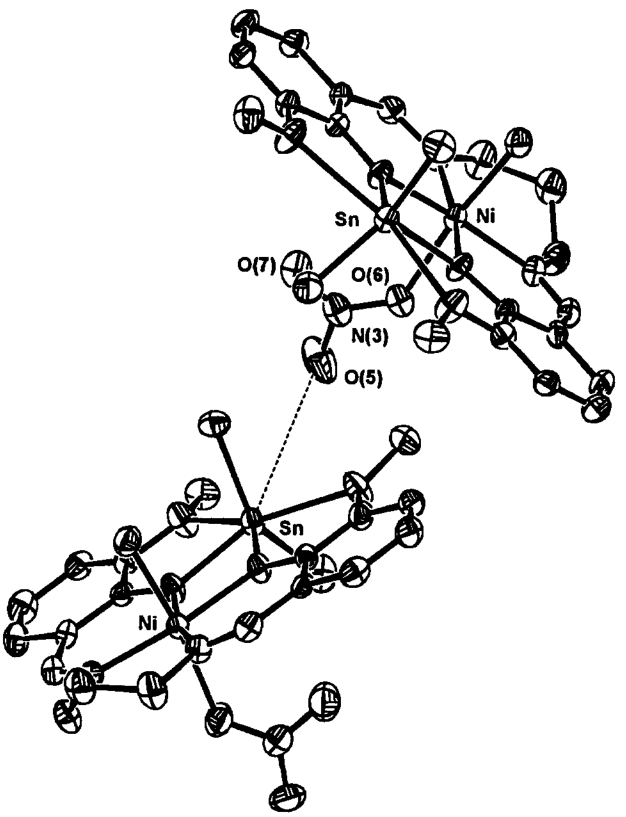

Fig. 5. Molecular association in **C** (the dotted line indicates an intermolecular contact).

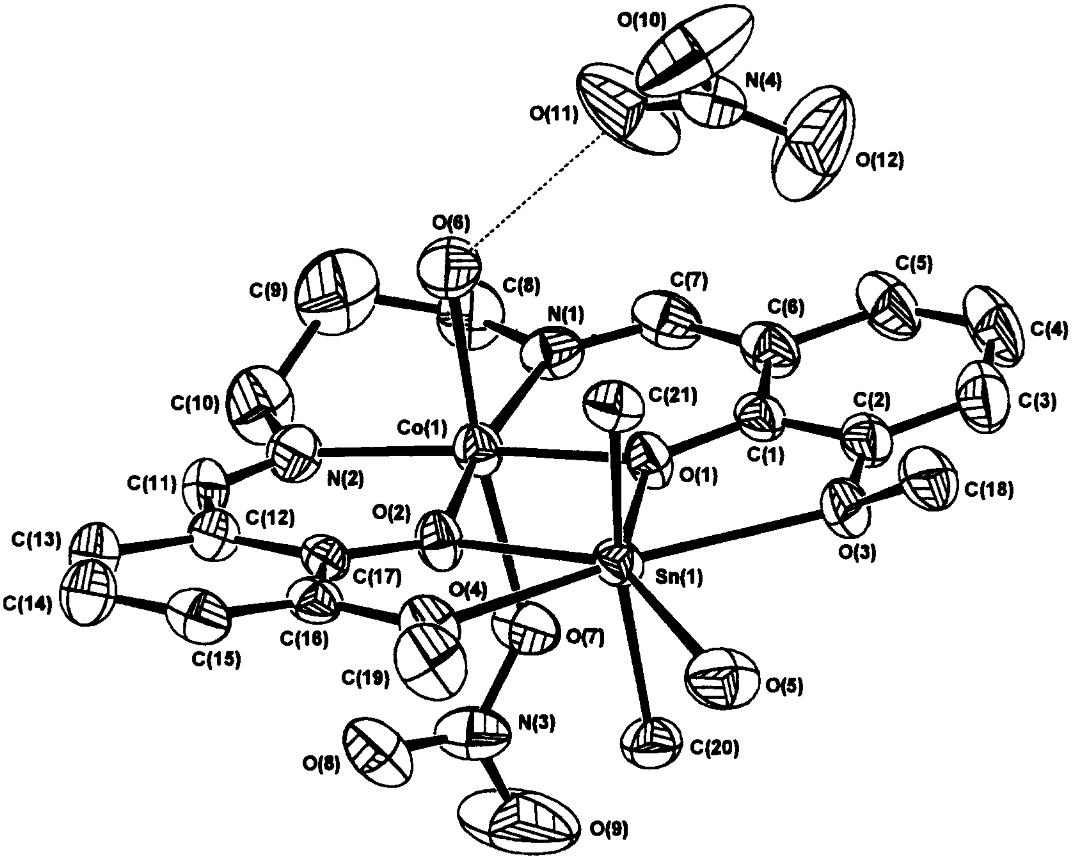

Fig. 6. The asymmetric unit of **D** (the dotted line indicates a hydrogen bonding interaction.

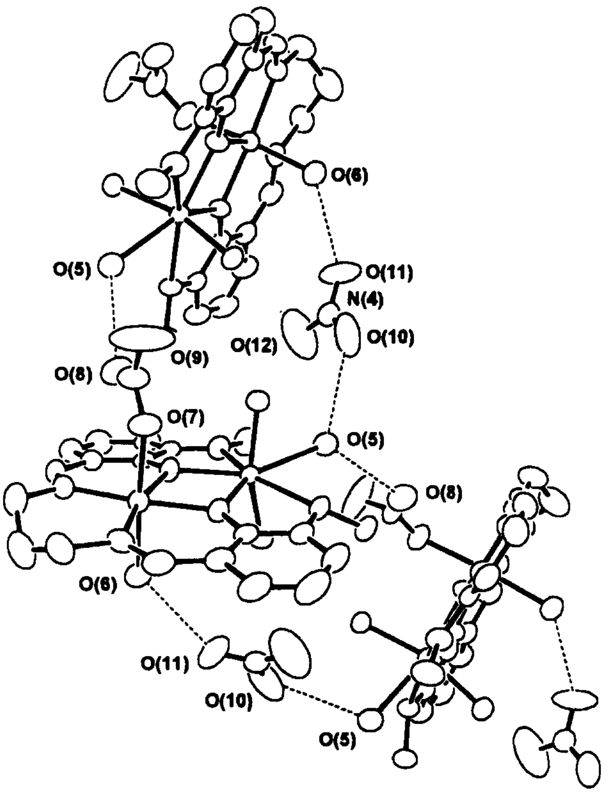

Fig. 7. Hydrogen bonding interactions (dotted lines) in **D**.

the transition metal or zinc. In this respect the complexes can all be considered as zwitterionic or intimate ion-paired bimetallics, hence the formulae shown in Tables 1 and 2. The structures differ in the roles of the second nitrate and water, which are present only in **C** and **D** (see Figs. 4 and 6 respectively).

Complexes **A** and **B** are isomorphous. In each case a nitrate group acts as a monodentate ligand to the metal in the inner O_2N_2 coordination site, thus giving the metal square pyramidal geometry. The second nitrate acts as a monodentate ligand to tin. The coordinating oxygen of this nitrate group, the phenolic and methoxy oxygens and tin are essentially coplanar, and this defines the equatorial plane of pentagonal pipyramidal geometry about tin. Bond angles about tin are, perhaps not surprisingly, remarkably similar in the two complexes. In particular, both the bond angles in the equatorial plane and the axial C–Sn–C bond angle in **A** differ by no more than 1° from the corresponding angles in **B**, and by no more than 2° from the corresponding values in $[SnPh_2(NCS)] \cdot [Ni(3MeO\text{-}sal1,3pn)(NCS)]^+$ [6]. In this latter complex a Sn–NCS donor bond takes the place of the Sn–nitrate donor bond in both **A** and **B**. The marked similarity between the coordination geometry about tin in both **A** and **B** and in $[SnPh_2(NCS)] \cdot [Ni(3MeO\text{-}sal1,3pn)(NCS)]^+$ is partly attributable to the fact that the Sn–O donor bond lengths (2.418 and 2.406

Å in **A** and **B**, respectively) involving the nitrate group are very similar to the Sn–NCS donor bond length (2.408 Å). The strength of these donor bonds influences both the position of tin within the outer O_4 coordination site of the salicylaldimine ligand and the C–Sn–C bond angle [6].

There are small, but noteworthy, differences between analagous bond lengths to tin in **A** and **B**. These can be traced to the nature of the metal in the inner O_2N_2 site. Cobalt forms one Co–O bond to a phenolic oxygen which is comparable in length (2.087(2) Å) to a Zn–O (phenolic oxygen) bond length (2.0860(13) Å). The phenolic oxygens in question thus form Sn–O bonds of comparable length (2.175(2) and 2.1795(12) Å in the case of the cobalt- and zinc-containing structures, respectively). By contrast, the second phenolic oxygen forms a Co–O bond of length 2.053(2) Å, which is considerably shorter than the comparable Zn–O bond (2.0990(3) Å), and as a consequence these phenolic oxygens form Sn–O bonds which are significantly different in length (2.190(2) and 2.1684(13) Å in the case of the cobalt- and zinc-containing structures, respectively), the shorter Sn–O bond being associated with the long metal–oxygen bond in the O_2N_2 site. Finally, as a consequence of the shorter average Sn–O bond length (involving the phenolic oxygens) in the zinc-containing structure the nitrate oxygen donor bond to tin (approximately *trans* to these bonds) is longer (2.418(2) Å) than the analagous bond (2.406(3) Å) in the cobalt-containing structure.

Table 7
Atomic coordinates ($\times 10^4$) for **D**

	x	*y*	*z*
Sn(1)	4535(1)	1739(1)	2024(1)
Co(1)	2825(1)	2424(1)	548(1)
O(1)	2605(3)	1574(2)	1330(2)
O(2)	4732(3)	2570(2)	1160(2)
O(3)	2788(4)	672(2)	2459(2)
O(4)	7049(3)	2382(3)	2013(2)
O(5)	5782(5)	1442(3)	3212(2)
O(6)	3673(4)	1178(3)	100(2)
O(7)	1832(4)	3587(3)	1033(2)
O(8)	3454(5)	4669(3)	1147(2)
O(9)	1565(7)	4926(5)	1498(5)
O(10)	4575(8)	−1901(6)	861(3)
O(11)	3478(8)	−783(4)	418(3)
O(12)	2879(7)	−1439(7)	1231(3)
N(1)	844(4)	2062(3)	65(2)
N(2)	3434(5)	3304(3)	−146(2)
N(3)	2282(6)	4404(4)	1218(3)
N(4)	3642(5)	−1372(3)	841(2)
C(1)	1486(5)	1047(3)	1417(2)
C(2)	1539(5)	552(3)	2012(3)
C(3)	440(6)	−16(4)	2133(4)
C(4)	−758(6)	−112(4)	1640(4)
C(5)	−824(6)	385(4)	1063(3)
C(6)	267(5)	980(4)	929(3)
C(7)	44(6)	1466(4)	289(3)
C(8)	300(6)	2483(5)	−587(3)
C(9)	1401(9)	2743(7)	−981(3)
C(10)	2398(7)	3554(5)	−735(3)
C(11)	4686(6)	3605(4)	−111(3)
C(12)	5889(5)	3438(3)	393(2)
C(13)	7189(6)	3790(4)	254(3)
C(14)	8412(6)	3656(5)	679(3)
C(15)	8431(5)	3175(4)	1265(3)
C(16)	7184(5)	2835(3)	1423(2)
C(17)	5895(5)	2941(3)	987(2)
C(18)	3210(7)	−132(4)	2888(3)
C(19)	8319(6)	2167(5)	2474(3)
C(20)	3820(6)	2906(4)	2525(3)
C(21)	5523(6)	463(4)	1803(3)

Table 8
Bond lengths (Å) and angles (deg) for **A**

Sn(1)–C(26)	2.143(2)	Sn(1)–C(33)	2.144(2)
Sn(1)–O(3)	2.1684(13)	Sn(1)–O(4)	2.1795(12)
Sn(1)–O(10)	2.418(2)	Sn(1)–O(2)	2.493(2)
Sn(1)–O(1)	2.4971(14)	Zn(1)–O(6)	2.026(2)
Zn(1)–N(2)	2.033(2)	Zn(1)–N(1)	2.070(2)
Zn(1)–O(4)	2.0860(13)	Zn(1)–O(3)	2.0990(13)
O(1)–C(2)	1.369(3)	O(2)–C(16)	1.379(3)
O(3)–C(1)	1.336(2)	O(4)–C(17)	1.331(2)
N(1)–C(7)	1.276(3)	N(1)–C(8)	1.473(3)
N(2)–C(11)	1.282(3)	N(2)–C(10)	1.472(3)
C(6)–C(7)	1.439(3)	C(8)–C(9)	1.506(4)
C(9)–C(10)	1.514(4)	C(11)–C(12)	1.445(3)
O(5)–N(3)	1.203(3)	O(6)–N(3)	1.237(3)
O(7)–N(3)	1.241(3)	O(8)–N(4)	1.213(4)
O(9)–N(4)	1.199(4)	O(10)–N(4)	1.300(3)
C(26)–Sn(1)–C(33)	168.75(9)	C(26)–Sn(1)–O(3)	97.56(8)
C(33)–Sn(1)–O(3)	92.62(8)	C(26)–Sn(1)–O(4)	92.87(7)
C(33)–Sn(1)–O(4)	95.06(7)	O(3)–Sn(1)–O(4)	70.39(5)
C(26)–Sn(1)–O(10)	84.53(8)	C(33)–Sn(1)–O(10)	84.40(7)
O(3)–Sn(1)–O(10)	144.30(6)	O(4)–Sn(1)–O(10)	145.30(6)
C(26)–Sn(1)–O(2)	83.77(8)	C(33)–Sn(1)–O(2)	91.95(9)
O(3)–Sn(1)–O(2)	137.58(5)	O(4)–Sn(1)–O(2)	67.21(5)
O(10)–Sn(1)–O(2)	78.12(6)	C(26)–Sn(1)–O(1)	89.99(7)
C(33)–Sn(1)–O(1)	89.45(8)	O(3)–Sn(1)–O(1)	67.72(5)
O(4)–Sn(1)–O(1)	138.02(5)	O(10)–Sn(1)–O(1)	76.67(6)
O(2)–Sn(1)–O(1)	154.48(5)	O(6)–Zn(1)–N(2)	110.78(10)
O(6)–Zn(1)–N(1)	114.55(10)	N(2)–Zn(1)–N(1)	96.72(8)
O(6)–Zn(1)–O(4)	93.28(8)	N(2)–Zn(1)–O(4)	88.84(6)
N(1)–Zn(1)–O(4)	147.07(7)	O(6)–Zn(1)–O(3)	92.49(8)
N(2)–Zn(1)–O(3)	151.76(7)	N(1)–Zn(1)–O(3)	87.35(7)
O(4)–Zn(1)–O(3)	73.56(5)	N(3)–O(6)–Zn(1)	118.4(2)
N(4)–O(10)–Sn(1)	124.9(2)		

Somewhat surprisingly, the coordination geometry about tin in **C** differs significantly from that in both **A** and **B** in that it does not feature the nitrate donor bond to tin that would complete the pentagonal bipyramidal coordination geometry. The absence of this donor bond causes the Sn–O bonds involving the phenolic oxygens to be significantly shorter than corresponding bond lengths in **A** and **B** (see Tables 8–10). However, the molecular alignment in the lattice of **C** (as shown in Fig. 5 for a pair of neighbouring molecules) brings an oxygen, O(5), of a nitrate group coordinated to nickel within 3.949 Å of tin. This type of alignment is very similar to that in $[SnBu^n_2]^{2+} \cdot [Ni(3MeO\text{-}sal2,3pn)(NCS)_2]^{2-}$ where a sulphur makes an intermolecular

Sn–S contact of 3.747 Å. Although the Sn–O contact is very long, it does appear to influence the C–Sn–C bond angle (this parameter being particularly sensitive to donor interactions directed between the methoxy oxygens). For example, the C–Sn–C bond angle of 135.3(3)° in $[\mathrm{SnMe_2}]^{2+}\cdot[\mathrm{Ni(3MeO\text{-}sal1,3pn)(NCS)_2}]^{2-}$, in which there are no intermolecular interactions with tin, is opened to 145.9(2)° in $[\mathrm{SnBu^n_2}]^{2+}\cdot[\mathrm{Ni(3MeO\text{-}sal2,3pn)(NCS)_2}]^{2-}$ and to 141.7(3)° in **C**.

The weakly associated chains resulting from the nitrate–tin interactions are linked by hydrogen bonding involving all of the water molecules coordinated to nickel and all of the uncoordinated nitrate groups. Each water forms a relatively strong hydrogen bond with O(9) belonging to one nitrate group and another with O(10) belonging to another nitrate group. These hydrogen bonding interactions result in contacts of 2.885 Å for O(8)–O(9) and 2.818 Å for O(8)–O(10); O(11) is not involved in significant hydrogen bonding interactions. The extensive hydrogen bonding generated in this fashion links every molecule within the chain generated by the tin–nitrate interactions with a molecule of each of two neighbouring chains.

The structure of **D** is similar to that of **C** in that it contains uncoordinated nitrate groups while, on the other hand, it is similar to those of **A** and **B** insofar as tin has pentagonal bipyramidal coordination geometry. This geometry is made possible in **D** as a result of a coordinated water molecule to tin. The tin–water donor bond, Sn(1)–O(5), is significantly longer (2.557(4) Å) than the tin–nitrate donor bonds lengths in **A** and **B** (average value of 2.412 Å), manifesting itself in the C–Sn–C bond angle being reduced by approximately 5.5° compared with angles in **A** and **B** and in the Sn–O bonds involving the phenolic oxygens being shorter than corresponding bonds in **A** and **B** (see Tables 7–9 and 11).

Table 9
Bond lengths (Å) and angles (deg) for **B**

Sn(1)–C(20)	2.139(3)	Sn(1)–C(27)	2.149(4)
Sn(1)–O(2)	2.175(2)	Sn(1)–O(1)	2.190(2)
Sn(1)–O(5)	2.406(3)	Sn(1)–O(3)	2.490(2)
Sn(1)–O(4)	2.493(2)	Co(1)–N(1)	2.039(3)
Co(1)–O(1)	2.053(2)	Co(1)–O(8)	2.074(4)
Co(1)–N(2)	2.077(3)	Co(1)–O(2)	2.087(2)
O(1)–C(1)	1.345(4)	O(2)–C(17)	1.331(4)
O(3)–C(2)	1.384(4)	O(4)–C(16)	1.376(4)
O(5)–N(3)	1.302(5)	O(6)–N(3)	1.202(5)
O(7)–N(3)	1.198(5)	O(8)–N(4)	1.197(5)
O(9)–N(4)	1.185(4)	O(10)–N(4)	1.232(5)
N(1)–C(7)	1.269(5)	N(1)–C(8)	1.478(4)
N(2)–C(11)	1.276(5)	N(2)–C(10)	1.477(5)
C(6)–C(7)	1.450(5)	C(8)–C(9)	1.519(6)
C(9)–C(10)	1.480(6)	C(11)–C(12)	1.442(5)
C(20)–Sn(1)–C(27)	168.95(14)	C(20)–Sn(1)–O(2)	97.44(12)
C(27)–Sn(1)–O(2)	92.61(12)	C(20)–Sn(1)–O(1)	93.07(11)
C(27)–Sn(1)–O(1)	94.64(12)	O(2)–Sn(1)–O(1)	70.23(8)
C(20)–Sn(1)–O(5)	84.51(12)	C(27)–Sn(1)–O(5)	84.65(12)
O(2)–Sn(1)–O(5)	144.26(9)	O(1)–Sn(1)–O(5)	145.48(9)
C(20)–Sn(1)–O(3)	83.97(12)	C(27)–Sn(1)–O(3)	91.74(13)
O(2)–Sn(1)–O(3)	137.38(8)	O(1)–Sn(1)–O(3)	67.15(8)
O(5)–Sn(1)–O(3)	78.36(9)	C(20)–Sn(1)–O(4)	89.91(11)
C(27)–Sn(1)–O(4)	89.70(13)	O(2)–Sn(1)–O(4)	67.52(8)
O(1)–Sn(1)–O(4)	137.67(8)	O(5)–Sn(1)–O(4)	76.83(9)
O(3)–Sn(1)–O(4)	154.90(8)	N(1)–Co(1)–O(1)	89.29(10)
N(1)–Co(1)–O(8)	109.6(2)	O(1)–Co(1)–O(8)	90.89(14)
N(1)–Co(1)–N(2)	96.19(13)	O(1)–Co(1)–N(2)	147.02(12)
O(8)–Co(1)–N(2)	117.3(2)	N(1)–Co(1)–O(2)	154.28(11)
O(1)–Co(1)–O(2)	74.67(8)	O(8)–Co(1)–O(2)	90.95(13)
N(2)–Co(1)–O(2)	87.37(11)	N(3)–O(5)–Sn(1)	125.1(2)
N(4)–O(8)–Co(1)	114.2(3)		

Table 10
Bond lengths (Å) and angles (deg) for **C**

Sn(1)–C(20)	2.104(8)	Sn(1)–O(1)	2.092(4)
Sn(1)–O(2)	2.092(4)	Sn(1)–C(21)	2.105(7)
Sn(1)–O(4)	2.511(5)	Sn(1)–O(3)	2.510(5)
Ni(1)–N(1)	2.002(6)	Ni(1)–N(2)	2.015(6)
Ni(1)–O(2)	2.020(4)	Ni(1)–O(1)	2.045(4)
Ni(1)–O(8)	2.088(5)	Ni(1)–O(6)	2.152(5)
O(1)–C(1)	1.361(7)	O(2)–C(17)	1.350(8)
O(3)–C(2)	1.397(8)	O(4)–C(16)	1.380(9)
O(5)–N(3)	1.226(9)	O(6)–N(3)	1.269(8)
O(7)–N(3)	1.227(9)	O(9)–N(4)	1.238(8)
O(10)–N(4)	1.230(8)	O(11)–N(4)	1.227(8)
N(1)–C(7)	1.278(9)	N(1)–C(8)	1.466(9)
N(2)–C(11)	1.280(9)	N(2)–C(10)	1.462(8)
C(6)–C(7)	1.436(10)	C(8)–C(9)	1.481(11)
C(9)–C(10)	1.519(11)	C(11)–C(12)	1.439(10)
C(20)–Sn(1)–O(1)	105.4(3)	C(20)–Sn(1)–O(2)	106.3(3)
O(1)–Sn(1)–O(2)	73.6(2)	C(20)–Sn(1)–C(21)	141.7(3)
O(1)–Sn(1)–C(21)	105.3(2)	O(2)–Sn(1)–C(21)	104.0(3)
C(20)–Sn(1)–O(4)	81.0(3)	O(1)–Sn(1)–O(4)	141.2(2)
O(2)–Sn(1)–O(4)	68.0(2)	C(21)–Sn(1)–O(4)	89.3(3)
C(20)–Sn(1)–O(3)	85.2(3)	O(1)–Sn(1)–O(3)	68.1(2)
O(2)–Sn(1)–O(3)	141.6(2)	C(21)–Sn(1)–O(3)	85.5(3)
O(4)–Sn(1)–O(3)	150.2(2)	N(1)–Ni(1)–N(2)	101.7(2)
N(1)–Ni(1)–O(2)	166.3(2)	N(2)–Ni(1)–O(2)	91.9(2)
N(1)–Ni(1)–O(1)	90.3(2)	N(2)–Ni(1)–O(1)	167.8(2)
O(2)–Ni(1)–O(1)	76.1(2)	N(1)–Ni(1)–O(8)	90.8(2)
N(2)–Ni(1)–O(8)	88.1(2)	O(2)–Ni(1)–O(8)	87.6(2)
O(1)–Ni(1)–O(8)	89.4(2)	N(1)–Ni(1)–O(6)	82.3(2)
N(2)–Ni(1)–O(6)	92.8(2)	O(2)–Ni(1)–O(6)	99.2(2)
O(1)–Ni(1)–O(6)	91.0(2)	O(8)–Ni(1)–O(6)	173.2(2)
N(3)–O(6)–Ni(1)	131.3(5)		

The hydrogen bonding in **D** is more complicated than that in **C** as a result of the extra molecule of water (coordinated to tin) in the former. The nitrate group bonded to nickel is involved in a hydrogen bonding interaction with the water bonded to tin in a neighbouring molecule. This interaction, predominantly involving O(8) of the nitrate group (see Fig. 7) results in an O(8)–O(5) contact of 2.829 Å. This interaction generates a hydrogen-bonded zig-zag chain, a section of which is shown in Fig. 7. The chain is further cemented by a second hydrogen bonding link between neighbouring molecules. The orientation of successive molecules along the chain is such that an uncoordinated nitrate

Table 11
Bond lengths (Å) and angles (deg) for **D**

Sn(1)–C(20)	2.095(5)	Sn(1)–C(21)	2.095(5)
Sn(1)–O(2)	2.147(3)	Sn(1)–O(1)	2.150(3)
Sn(1)–O(3)	2.516(3)	Sn(1)–O(5)	2.557(4)
Sn(1)–O(4)	2.585(3)	Co(1)–O(1)	2.029(3)
Co(1)–N(2)	2.035(4)	Co(1)–O(2)	2.050(3)
Co(1)–N(1)	2.056(4)	Co(1)–O(6)	2.180(4)
Co(1)–O(7)	2.198(4)	O(1)–C(1)	1.340(6)
O(2)–C(17)	1.335(5)	O(3)–C(2)	1.391(6)
O(4)–C(16)	1.386(6)	O(7)–N(3)	1.251(6)
O(8)–N(3)	1.219(7)	O(9)–N(3)	1.209(7)
O(10)–N(4)	1.156(7)	O(11)–N(4)	1.181(7)
O(12)–N(4)	1.178(7)	N(1)–C(7)	1.268(7)
N(1)–C(8)	1.470(7)	N(2)–C(11)	1.267(7)
N(2)–C(10)	1.469(7)	C(6)–C(7)	1.457(8)
C(8)–C(9)	1.483(10)	C(9)–C(10)	1.509(10)
C(11)–C(12)	1.434(7)		
C(20)–Sn(1)–C(21)	163.3(2)	C(20)–Sn(1)–O(2)	94.1(2)
C(21)–Sn(1)–O(2)	99.7(2)	C(20)–Sn(1)–O(1)	95.0(2)
C(21)–Sn(1)–O(1)	98.1(2)	O(2)–Sn(1)–O(1)	72.62(11)
C(20)–Sn(1)–O(3)	89.2(2)	C(21)–Sn(1)–O(3)	86.3(2)
O(2)–Sn(1)–O(3)	140.07(12)	O(1)–Sn(1)–O(3)	67.45(12)
C(20)–Sn(1)–O(5)	78.4(2)	C(21)–Sn(1)–O(5)	84.9(2)
O(2)–Sn(1)–O(5)	141.02(13)	O(1)–Sn(1)–O(5)	145.52(14)
O(3)–Sn(1)–O(5)	78.57(13)	C(20)–Sn(1)–O(4)	97.1(2)
C(21)–Sn(1)–O(4)	80.1(2)	O(2)–Sn(1)–O(4)	65.94(11)
O(1)–Sn(1)–O(4)	137.44(12)	O(3)–Sn(1)–O(4)	152.94(11)
O(5)–Sn(1)–O(4)	77.02(13)	O(1)–Co(1)–N(2)	169.0(2)
O(1)–Co(1)–O(2)	77.20(12)	N(2)–Co(1)–O(2)	91.9(2)
O(1)–Co(1)–N(1)	91.4(2)	N(2)–Co(1)–N(1)	99.5(2)
O(2)–Co(1)–N(1)	168.4(2)	O(1)–Co(1)–O(6)	88.22(14)
N(2)–Co(1)–O(6)	90.5(2)	O(2)–Co(1)–O(6)	88.6(2)
N(1)–Co(1)–O(6)	89.3(2)	O(1)–Co(1)–O(7)	87.6(2)
N(2)–Co(1)–O(7)	94.3(2)	O(2)–Co(1)–O(7)	93.70(14)
N(1)–Co(1)–O(7)	87.5(2)	O(6)–Co(1)–O(7)	174.6(2)
N(3)–O(7)–Co(1)	130.4(3)		

group can insert itself between the water bonded to tin in one molecule and the water bonded to nickel in the neighbouring molecule, and become involved in hydrogen bonding with both water molecules. This results in an O(6)–O(11) contact of 2.813 Å (see Figs. 6 and 7) and an O(5)–O(10) contact of 3.037 Å (see Fig. 7). Hydrogen bonded chains such as that shown in Fig. 7 are linked through further hydrogen bonding interactions involving O(10) and O(11) and a water molecule coordinated to nickel, thus providing O(10)–O(6) and O(11)–O(6) contacts of 2.979 and 3.163 Å, respectively (these interactions including the same water molecule).

The complex $[SnPh_2(NO_3)] \cdot [Co(3MeO\text{-}sal1,3pn)(NO_3)]$ is so formulated on the following basis. It contains high-spin cobalt (see the magnetic data in Table 2) and thus does not contain square-planar cobalt. Since the complex does not contain water, there must be at least one cobalt–nitrate bond. The Sn-119 Mössbauer quadrupole splitting of 3.71 mm s^{-1} points to a C–Sn–C bond angle much greater than that anticipated for the trapezoidal geometry which would exist about tin in the absence of a tin–nitrate donor bond [6]. Thus, it seems very likely that a nitrate group remains coordinated to tin, and that the complex is isostructural with **A** and **B**.

When dimethyltin dinitrate was treated with Ni (3MeO-sal1,3pn) in acetone a paramagnetic moss-green complex was obtained, contrasting with the pale blue paramagnetic complex (**C**) obtained from the reaction in acetonitrile. The IR-spectrum of the green complex clearly suggested the presence of either coordinated or lattice water, while at the same time a band at ca. 1650 cm^{-1} (not in the spectrum of the blue adduct) was consistent with coordinated acetone. In fact, analytical data (see Table 1) were consistent with the presence of two molecules of acetone in a 1/1 addition complex. The very large Sn-119 Mössbauer quadrupole splitting of 4.59 mm s^{-1} for the green adduct (contrasting with a value of 3.93 mm s^{-1} for **C**) points to a C–Sn–C bond angle close to 180°, and this in turn points to a seven-coordinate tin environment [6]. Bearing in mind that the IR spectrum showed evidence for coordinated and not uncoordinated acetone, it would appear that acetone molecules are coordinated to tin and nickel and that the water molecule is a lattice molecule.

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