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Journal of Organometallic Chemistry 614–615 (2000) 283–293

Journal of Organometallic Chemistry

New hexacyclic binuclear tin complexes derived from bis-(3,5-di-*tert*-butyl-2-phenol)oxamide

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Received 30 May 2000

Dedicated to Professor Sheldon Shore on the occasion of his 70th birthday.

Abstract

The syntheses of bis-(3,5-di-*tert*-butyl-2-phenol)oxamide (**2a**) and four new hexacyclic bimetallic tin compounds derivatives are reported: bis-(3,5-di-*tert*-butyl-2-oxo-phenyl)-oxamido-bis(dibutyltin) (**3**), bis-(3,5-di-*tert*-butyl-2-oxo-phenyl)-oxamido-bis-(diphenyltin) (**4**), bis(triethylammonium) bis-(3,5-di-*tert*-butyl-2-oxo-phenyl)-oxamido-bis-(dichlorobutyl-stannate) (**5**), and bis-[(O–Sn) ethanol]-bis-(3,5-di-*tert*-butyl-2-oxo-phenyl)-oxamido-bis-(chlorophenyltin) (**6**). All tin compounds show a planar ligand skeleton in which each tin atom is linked to the phenoxy group, to the anilinic nitrogen atom and to the oxygen of the oxamide group. Compounds **3** and **4** have two pentacoordinated diorganyl tin atoms with a distorted bpt geometry, whereas **5** contains a dianionic structure with two hexacoordinated tin atoms bonded to a *n*-butyl group and to two chlorine atoms and two triethyl ammonium as counterions. Compound **6** has two hexacoordinated tin atoms, each atom is bonded, in addition to the ligand, to one phenyl and one chlorine and coordinated to an ethanol molecule. Characterization of the compounds was made through usual analytical and spectroscopic methods. Structures of 4,6-di-*tert*-butyl-1-phenol-2-amine **1**, the oxamide **2a** and the four tin compounds **3**–**6** were established by the X-ray diffraction analyses. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Hexacyclic binuclear tin complexes ; Bis-(3,5-di-*tert*-butyl-2-phenol)oxamide

1. Introduction

We are interested in the preparation of main group derivatives of phenolamines [1–8]. These molecules are particularly relevant due to their rich oxidation–reduction chemistry which allows the preparation of different types of coordination compounds [9–20]. As a consequence of their easiness to coordinate Lewis acids, they give very rigid and stable heterocyclic molecules which are suitable models for structural and spectroscopic investigation (Fig. 1). In particular phenolamines give stable derivatives with tin compounds [7,18–20], some examples are shown in Fig. 2.

In continuing with our research, we decided to prepare the bis-(3,5-di-*tert*-butyl-2-phenol)-oxamide (**2a**) and to study its reactions with organometallic tin compounds. Interest in this investigation is based on several different structures that could be expected due to the polyfunctional nature of the ligand. In addition to the different possible coordination numbers for the tin atom and that the ligand could be found in different oxidation states in the reaction products depending on the tin substitution [7,8,20]. Another point of interest in the preparation of the tin compounds derived from phenolamines is based on the biocidic properties of the diphenolamine **2b** [21] and the potential activity of tin compounds as anticancer agents [22–25].

2. Results and discussion

Herein, we report the synthesis of the 4,6-di-*tert*-butyl-1-phenol-2-amine **1** the bis-(3,5-di-*tert*-butyl-2-phe-

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PII: S0022-328X(00)00689-6

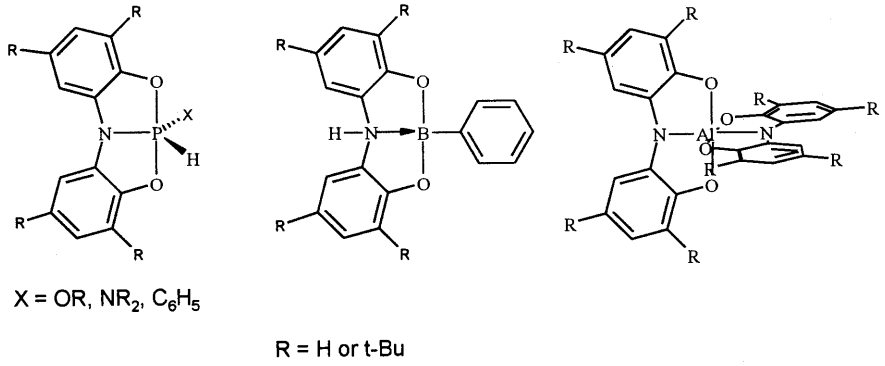


Fig. 1. Heterocycles derived from bis-(2-phenol)amine [3,6,8].

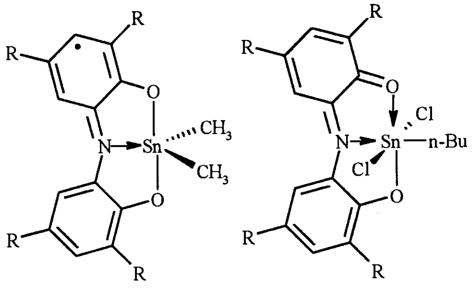


Fig. 2. Tin compounds derived from bis-(3,5-di-*tert*-butyl-2-phenol)-amine, R = *t*-Bu [7].

nol)-oxamide **2a** and the preparation of its binuclear hexacyclic compounds bearing penta- or hexacoordinated tin atoms: bis-(3,5-di-*tert*-butyl-2-oxo-phenyl)-oxamido-bis-(dibutyltin) (**3**), bis-(3,5-di-*tert*-butyl-2-oxo-phenyl)-oxamido-bis-(diphenyltin) (**4**), bis-(triethylammonium) bis-(3,5-di-*tert*-butyl-2-oxo-phenyl)-oxamido-bis-(dichlorobutyl-stannate) (**5**), and bis-[(O–Sn)-ethanol]-bis-(3,5-di-*tert*-butyl-2-oxo-phenyl)-oxamido-bis-(chlorophenyltin) (**6**), as well as the X-ray diffraction analyses of compounds **1**, **2a**, and **3**–**6**.

In order to prepare the oxamide **2a** we had first to synthesize the 4,6-di-*tert*-butyl-1-phenol-2-amine **1**. The synthesis of **1** from the reduction reaction of the 4,6-di-*tert*-butyl-benzo-2-iminoquinone and its NMR characterization are known [26]. We have prepared compound **1** by a different method: using the deamination reaction of ethylenediamine by the 3,5-di-*tert*-butyl-benzoquinone, (Fig. 3). The structure of **1** was characterized by spectroscopic methods and by an X-ray diffraction study (Fig. 4 and Tables 1, 3, 5–7). The molecular structure of 4,6-di-*tert*-butyl-1-phenol-2-amine **1** has normal parameters for a phenolamine, an intramolecular hydrogen bond has been found between the OH proton and the nitrogen (2.352 Å), but not intermolecular interactions (Fig. 4, Tables 5 and 7). The synthesis of compound **1** is not in agreement with a literature report [27] which establishes that the reaction of the 3,5-di-*tert*-butyl-benzoquinone with ethylenediamine gives the bis-(2-phenolamine)-1,2-ethylene.

Compound **1** was reacted with diethyloxalate to give compound **2a**. It was characterized by the common spectroscopic methods, the assignment of its NMR data (Tables 1 and 3), was based on HETCOR C/H and N/H and COSY experiments. ^{1}H-NMR variable temperature experiments were used to estimate the nature of the hydrogen bond having in mind that the N–H hydrogen bonds are a model of metallic coordination, the method is based on the shift calculations of the labile hydrogen atom resonance at different temperature [28]). Calculations for **2a** shows $\Delta\delta/\Delta T$ for N–H -4.65×10^{-3} ppm K^{-1} and for O–H -3.9×10^{-3} ppm K^{-1} which means weak intramolecular coordination of these protons, and a fast exchange with the solvent. The contrast with bis-(2-phenol)-oxamide **2b** is interesting [28,29] because **2b** presents a strongly bonded tricoordinated hydrogen atom in a planar molecular array, with carbonyl groups in *trans* position. ^{1}H-NMR experiments evidenced $\Delta\delta/\Delta T = -0.5\times10^{-3}$ ppm K^{-1} for N–H and -6.5×10^{-3} ppm K^{-1}

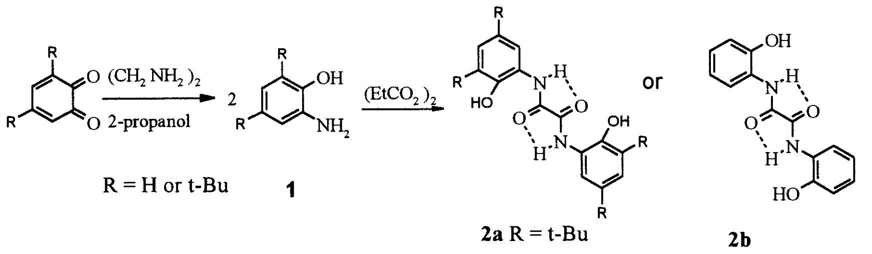


Fig. 3. Synthesis of bis-(3,5-di-*tert*-butyl-2-phenol)-oxamide **2a** and bis-(2-phenol)-oxamide **2b** [28,29].

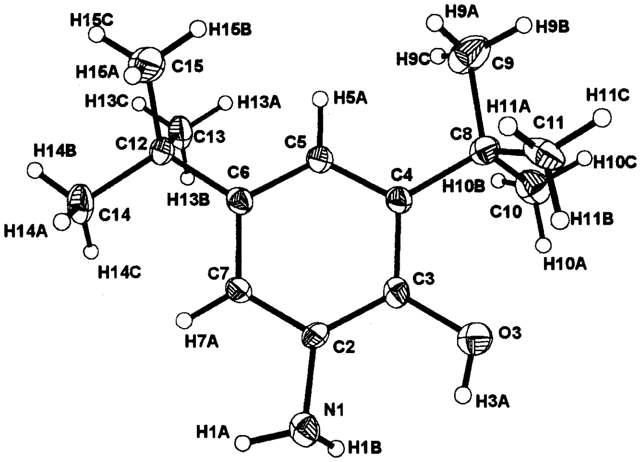


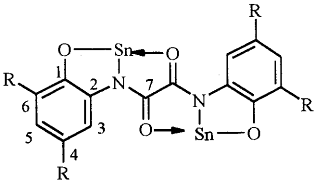
Fig. 4. Molecular structure of compound **1**.

for O–H, the same situation was found in the solid state by the X-ray diffraction study [29] ((N–H···O–H 2.172(2), N–H···O=C 2.138(2) Å). The solid state structure of **2a** (Fig. 5, Tables 5–7) is consistent with the structure in solution, it has a *trans* conformation for the oxamide group, the C1–O1 bond length is short (1.236(1) Å) whereas the N1–C1 bond is longer (1.323(3) Å). The proton is bonded to the nitrogen atom, the distance of N–H proton to the *cis* carbonyl oxygen atom O1 is 1.72 Å indicating a strong hydrogen bond. The oxygen atom of the phenolic group is not on the same side of the N–H group [29] and the phenol ring is not coplanar with the oxamide unit as is in the case of ligand **2b**.

The reactions of **2a** with dichloro-di-*n*-butyltin, dichloro-diphenyltin, trichloro-*n*-butyltin and trichloro-phenyltin in ethanol gave only one product, compounds **3**–**6**, respectively, which were microcrystalline solids, Figs. 6–7. The characterization was performed by the usual spectroscopic and X-ray diffraction analyses, Figs. 8–13. It was found that the ligand gave in all cases dinuclear derivatives, with the skeleton of the ligand in a planar array. The ligand **2a** was also reacted with dichlorodimethyltin and the binuclear compound of analogous structure to compounds **3** and **4** was submitted to an extensive NMR study [32].

All compounds gave good NMR spectra, Tables 1–4. The ^{119}Sn-NMR data is indicative of the coordination number of the tin atoms in solution [30,31], Table 1, for a similar compound bis-(3,5-di-*tert*-butyl-2-oxo-phenyl)-oxamido-bis-(dibutyltin) [32], it was found that the ^{119}Sn chemical shift was the same in the solid state (-83.6 ppm) than in solution (-85.5 ppm), indicating that in both the tin atom is pentacoordinated. By comparison with this chemical shifts, it is deduced that compounds **3** and **4**, derived from diorganyltin reagents, have pentacoordinated tin atoms ($\delta = -120.5$ for **3** and -257.5 for **4**) whereas in compounds **5**–**6** they are hexacoordinated ($\delta = -390.0$ for **5** and -257.0 for **6**). It should be noted that **4** and **6** have the same chemical shift but different substitutents at tin atom. Assignment of ^{1}H- and ^{13}C- data of compounds **3**–**6** was based on the values of the coupling constants $^{n}J(^{117/119}\text{Sn}–^{13}\text{C})$ [30–32] and by comparison with other phenolamine derivatives and by HETCOR and COSY experiments (Tables 1–4). ^{1}H- and ^{13}C-NMR data of the ionic compound **5** shows that two triethyl ammonium ions are present, whereas compound **6** contains a coordinated ethanol molecule. One interesting feature of the ^{1}H-NMR spectra of compounds **3**–**6** is the shifting to

Table 1
^{119}Sn-, ^{15}N- and ^{1}H-NMR data (CDCl$_3$)



Compound	^{119}Sn	^{15}N	^{1}H					
			H3	H5	2-*t*-bu	4-*t*-bu	OH	NH
1			6.93	6.83	1.30	1.43	3.28	3.28
2		-255	7.31	7.14	1.31	1.47	7.56	9.56
3	-120.5		8.44	7.18	1.36	1.45		
4	-257.5		8.65	7.31	1.44	1.62		
5	-390.0		8.26	7.09	1.31	1.43		8.33
6	-257.0		8.39	7.19	1.35	1.50	9.93	

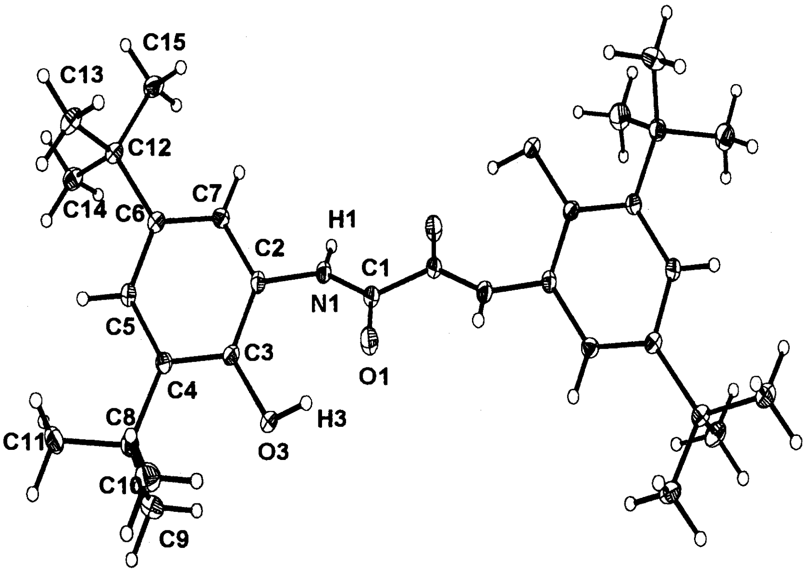
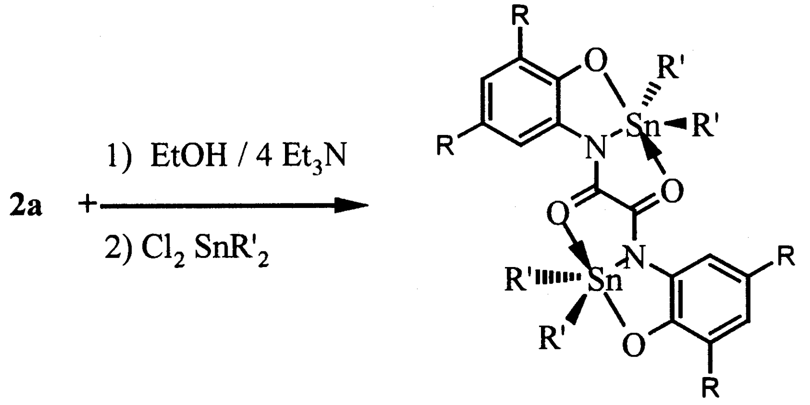


Fig. 5. Molecular structure of compound **2a**.

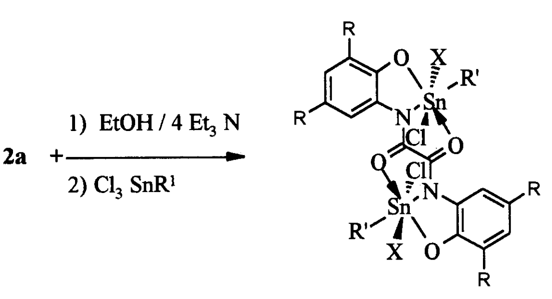


3: R’= *n*-Bu, R = *t*-Bu
4: R’= Ph, R = *t*-Bu

Fig. 6. Syntheses of compounds **3** and **4**.

higher frequency for the aromatic H3 atoms due to their interaction with the lone pairs of the carbonyl groups, Table 1. The same interaction was observed at the molecular structures in the solid state.

X-ray diffraction studies of **3**–**6** show that all molecules contain two tin atoms and a planar hexocyclic skeleton. Molecular structures of **3**–**5** feature a symmetric arrangement of the substitutents with respect to the plane of the molecule and have a symmetry C_2 axis whereas **6** does not has a plane but a S_2 improper axis. Tin atoms are always linked to oxygen atoms from the phenol and carbonyl groups, as well as to the anilinic nitrogen atom. The C–C bond lengths of the benzenic ring very near to those of an aromatic ring and O3–C3 and N1–C2 (sp^2–sp^2) single bond character



5: R’= *n*-Bu, R = *t*-Bu X= Cl
6: R’= Ph R = *t*-Bu X= EtOH

Fig. 7. Syntheses of complexes **5** and **6**, compound **5** is a dianion and is accompanied of two triethylammonium cations, **6** is coordinated to one ethanol molecule.

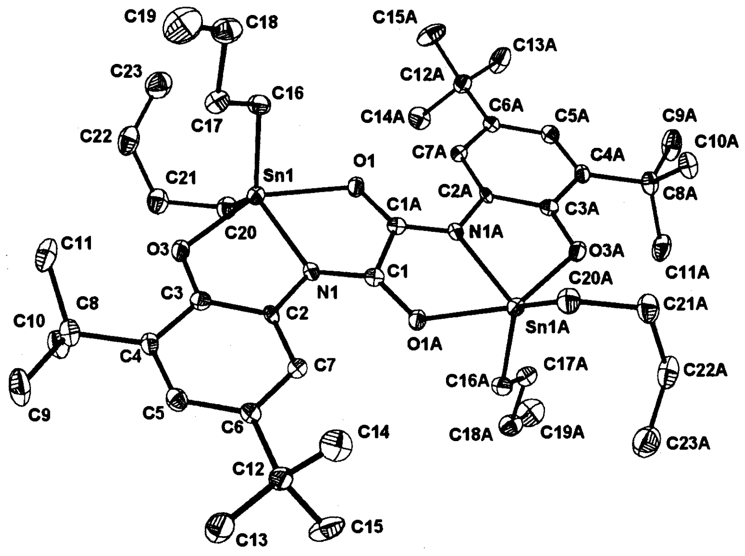


Fig. 8. ORTEP diagram of the molecular structure of compound **3**.

1.336–1.376 and 1.408–1.432 Å, respectively (Table 5) exclude a quinone structure of an oxidated ligand. The oxamide group represents a delocalyzed system with O1–C1A and C1–N1 having short bond lengths (in the range 1.271–1.280, and 1.282–1.323 Å, respectively) and with C1–C1A forming a single bond (1.52–1.526 Å). The bond lengths O–Sn show that tin atoms are covalently bonded to the phenol oxygen atoms (Sn–O3 2.02–2.07 Å) and coordinated to the carbonyl groups (Sn–O1 2.13–2.23 Å). The bond angles show that tin atoms in compounds **3**–**4** are present in a distorted bpt geometry [4]. In all compounds the angle O–Sn–O is found in the range between 150.3(8) and 153.5(4) probably due to the ligand tension. In compounds **3**–**4** the organyl groups in equatorial position have a wide angle (C–Sn–C 128.9(1)–129.7(4)). Compound **3** does not present intermolecular interactions but short contacts between some protons of the aromatic ring and of the methyl groups and oxygen lone pairs (H7A–O1 2.334; H10C–O3 2.351; H11C–O3 2.332 Å and their symmetrical counterparts). For compound **4** the cell has two molecules of the compound with four of $CHCl_3$, there are no intermolecular interactions, but only intramolecular hydrogen bonds between the protons of the aromatic ring, of the methyl and phenyl groups and the oxygen lone pairs (H7A–O1 2.384; H9C–O3 2.410; H10B–O3 2.355; H23A–O1 2.672; H27A–O3 2.607, H17A–O1 2.609 Å). Tin atoms in **5**–**6** display a distorted octahedral geometry, Figs. 10–13. In both compounds the organyl group lies in the molecular plane, the two chlorides or the chloride and the ethanol groups are in *trans* position. Compound **5** is ionic, the metallic complex being a dianion and bearing two triethyl ammonium cations. The two Sn–Cl distances in **5** are not equivalent (Sn–Cl2 2.429(1) and Sn–Cl1 2.593(1) Å), one of the chloride atoms has a longer bond length due to a short N–H···Cl interaction (2.22

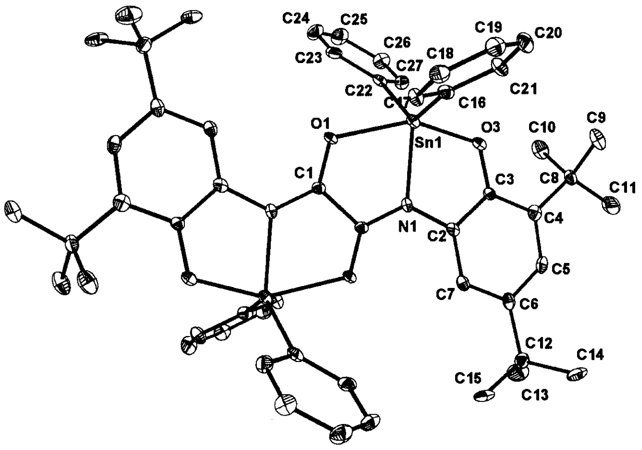


Fig. 9. Molecular structure of compound **4**.

Table 2
^1H-NMR data of Sn substituents

Compound	α-CH_2	β-CH_2	γ-CH_2	CH_3
3	1.73	1.55	1.43	0.93
5 [a]	2.09	1.57	1.42	1.0
	o-	*m*,-*p*		
4	7.9	7.40		
6 [b]	8.1	7.46		

[a] $NHEt_3^+$: CH_2 2.76, CH_3 0.98.

[b] OEt CH_2 3.0, CH_3 1.20.

Table 3
^{13}C-NMR data (CDCl$_3$) ($^nJ(^{13}C–^{119/117}Sn)$)

Compound	C1	C2	C3	C4	C5	C6	CO	*t*-bu quater.	*t*-bu CH$_3$
1	143.0	132.9	116.0	144.4	117.4	136.4		34.7, 35.1	30.2, 32.0
2	143.3	124.0	117.7	145.8	123.2	139.8	157.3	34.4, 35.4	29.9, 31.5
3	154.5 (25)	128.6 (42)	115.8 (23)	137.5	122.2	136.9	159.2 (42)	34.8, 35.6	29.0, 32.1
4	153.6 (22)	127.9 (50)	115.8 (28)	138.4	122.6	137.3 (16)	158.0 (55)	34.5, 35.4	29.7, 31.7
5	152.4 (35)	126.5 (77)	116.1 (50)	137.3	122.0	137.1	155.2 (94)	35.6, 36.2	29.8, 32.2
6	153.7	128 (52)	115.9 (33)	138.5	123.3	137.6 (13)	158.3	34.7, 35.8	30.1, 32.1

Å) and a weaker C–H···Cl (2.74 Å) of two Et$_3$NH cations as is shown in Fig. 11. Hydrogen contacts with oxygen atoms were also found (H7A–O1 2.323; H9A–O3 2.320; H11A–O3 2.386 Å). Compound **6** crystallized with two ethanol molecules and presents intermolecular hydrogen bonds, the OH proton of the coordinated ethanol is bonded to the oxygen of one free ethanol (H2A–O4 1.831 Å) and the OH of one free ethanol is bonded to the chlorine atom (H4A–Cl 2.653 Å). There are contacts between the chlorine atoms (Cl–Cl 3.511 Å), Figs. 12 and 13. There are also intramolecular hydrogen bonds similar to those found in the previously discussed molecules (H7A–O1 2.385 Å). The tin geometries in compounds **3** and **5** are similar to those of diphenolamine derivatives, Fig. 2 [7].

In conclusion, we report that the reactions of bis-(3,5-di-*tert*-butyl-2-phenol)-oxamide **2a** with diorganyldichlorotin and organyltrichlorotin reagents gave selectively in all the reactions only one compound with two tin atoms penta- or hexa-coordinated. Tin compounds were moisture stable. The skeleton of the ligand was found linked to two tin atoms in an hexacyclic symmetric planar array. The ligand presents in all compounds a phenolic instead of a paramagnetic quinone structure and the NMR data could be obtained, the solid state structures of the tin compounds were retained in solution as was deduced by the spectroscopic data.

3. Experimental

Tin reagents and 3,5-di-*tert*-butyl-1,2-benzoquinone were commercially available. All reactions were performed with freshly distilled solvents. Melting points were obtained on a Mel-Temp II apparatus and are uncorrected. IR spectra were recorded on an FT-IR 1600 Perkin Elmer spectrophotometer using KBr pellets in the 4000–400 cm^{-1} range. Mass spectra in the EI mode were recorded at 20 eV on a Hewlett–Packard HP 5989 spectrometer. Fast atom bombardment mass spectrometry (FAB+ mass) was performed on a Jeol SX102A instrument of inverted geometry, in a matrix of 3-nitrobenzyl alcohol and in the 0–2200 *m*/*z* range. Elemental Analyses were performed by Oneida Research Services, Whitesboro, New York. NMR spectra were obtained on a Jeol GSX-270 ^{15}N (27.25 MHz), ^{119}Sn (100.73); Jeol Eclipse 400 MHz ^{15}N (40.51 MHz), ^{119}Sn (149.05), Bruker Advance 300 MHz ^{15}N (30.42 MHz), ^{119}Sn (111.92). The X-ray diffraction studies of compounds **1**, **5** and **6** were performed with an Enraf–Nonius CAD4 diffractometer (λ(Mo–K$_\alpha$) = 0.71073 Å). The X-ray diffraction study of compounds **2**–**4** was performed with a Siemens P4 instrument equipped with a CCD area detector and a low temperature device LTP2. Relevant crystallographic data are summarized in Tables 5 and 6. Structure solution and refinement were performed with the program SHELXL-97. Absorption correction (SADABS for **2**–**4** and SEMIEMPIRICAL for **5** and **6**).

3.1. 4,6-Di-tert-butyl-1-phenol-2-amine (1)

A solution of 8.0 g (36.3 mmol) of 3,5-di-*tert*-butyl-1,2-benzoquinone in 2-propanol (70 ml) was added to 9 ml of 1,2-ethylenediamine (70% in water) and

Table 4
^{13}C-NMR data, Sn-substituents ($^nJ(^{13}C–^{119/117}Sn)$)

Compound	α-CH$_2$	β-CH$_2$	γ-CH$_2$	CH$_3$
3	21.3 (576/550)	27.6 (27)	27.1 (84)	14.1
5 [a]	36.5 (1130/1082)	27.5(63)	25.8 (173.3/165.3)	14.3
	i-	*o*-	*m*-	*p*-
4	138.2 (955/913)	136.5 (46)	129.2 (86)	131.0 (17)
6 [b]	138.2	136.5 (54)	129.5 (84)	131.1 (16)

[a] NHEt$_3^+$ 46.1, 8.6.

[b] OEt 59.9, 17.5.

Table 5
Selected bond lengths (Å) of compounds **1**–**6**

	1	**2**	**3**	**4**	**5**	**6**
Sn–O1			2.230(2)	2.22(1)	2.172(3)	2.132(3)
Sn–O3			2.071(2)	2.07(1)	2.049(3)	2.020(4)
Sn–O2						2.287(4)
Sn–N			2.145(2)	2.15(1)	2.139(3)	2.142(4)
Sn–C			2.122(4) (C20)	2.12(1) (C22)	2.120(5)	2.112(5)
Sn–C			2.119(3) (C16)	2.14(1) (C16)		
C3–O3	1.355(5)	1.376(1)	1.351(4)	1.34(1)	1.336(5)	1.340(6)
C1A–O1		1.236(1)	1.271(4)	1.28(1)	1.280(4)	1.278(6)
C2–N1	1.400(7)	1.432(2)	1.419(4)	1.41(1)	1.408(5)	1.409(6)
N1–C1		1.323(3)	1.303(4)	1.31(1)	1.282(5)	1.283(6)
C1–C1A		1.532(3)	1.526(6)	1.52(2)	1.523(7)	1.524(9)
C2–C3	1.394(7)	1.395(2)	1.403(5)	1.41(1)	1.402(5)	1.405(7)
C3–C4	1.413(7)	1.400(2)	1.416(5)	1.43(1)	1.412(5)	1.409(7)
C4–C5	1.390(7)	1.394(2)	1.399(5)	1.39(1)	1.376(5)	1.383(7)
C5–C6	1.406(7)	1.401(2)	1.385(4)	1.40(1)	1.391(6)	1.393(7)
C6–C7	1.382(7)	1.375(2)	1.386(4)	1.38(1)	1.388(5)	1.376(7)
C7–C2	1.381(6)	1.393(2)	1.388(4)	1.39(1)	1.387(5)	1.381(7)

the mixture was refluxed for 2 h. The solvent was removed at reduced pressure. Then the solid was suspended in *n*-hexane and filtered to give 6.0 g (75%) of a colorless crystalline powder. It was recrystallized from toluene–ethanol (8:2). M.p. 165–167°C. MS; (EI, 20 eV) *m*/*z* [M$^+$] 221. IR (KBr) ν(cm^{-1}) 3367, 3290, 2714, 2598, 1594, 1491, 1420, 1359, 1314, 1235, 951. Anal. Found: C, 75.81; H, 10.32; N, 6.39. Calc. for $C_{14}H_{23}NO$: C, 75.98; H, 10.46; N, 6.32%.

3.2. *Bis-(3,5-di-tert-butyl-2-phenol)-oxamide* (**2a**)

A mixture of 0.5 g (2.3 mmol) of 3,5-di-*tert*-butyl-1,2-phenolamine and 1.2 ml of diethyloxalate (9 mmol) was heated at 80°C for 1.5 h. The solid was suspended in *n*-hexane and filtered to give 0.88 g (80%) of a yellow crystalline powder. It was recrystallized from ethanol–CH_2Cl_2 (8:2). M.p. 198–200°C. MS; (EI, 20 eV) *m*/*z* [M$^+$] 496, IR (KBr) ν(cm^{-1}): 1662, 1514, 1477, 1235, 1359, 1314, 1235, 951. Anal. Found: C, 72.49; H, 9.08; N, 5.59. Calc. for $C_{30}H_{44}N_2O_4$: C, 72.54; H, 8.92; N, 5.63%.

3.3. *General procedure for* **3**–**6**

3.3.1. *Bis-(3,5-di-tert-butyl-2-oxo-phenyl)-oxamido-bis-(dibutyltin)* (**3**)

A solution of 0.5 g (1 mmol) of **2a** in ethanol (10 ml) and triethylamine (0.25 ml, 2 mmol) was mixed with a solution of dichoro-di-*n*-butyltin(IV) (0.63 g 2 mmol) in ethanol (5 ml). After 15 min the solid was filtered and washed with *n*-hexane. An orange microcrystalline powder was obtained (0.95 g, 98%). Single crystals were obtained from ethanol–CH_2Cl_2 (3:2). M.p. 168–170°C. MS; (FAB +) *m*/*z* [M$^+$] 961. IR (KBr) ν(cm^{-1}): 1600, 1480, 1410, 1380, 1300, 1280. Anal. Found: C, 56.79; H, 7.70; N, 3.20. Calc. for $C_{46}H_{76}N_2O_4Sn_2 1/8CH_2Cl_2$: C, 57.16; H, 7.93; N, 2.90%.

3.3.2. *Bis-(3,5-di-tert-butyl-2-oxo-phenyl)-oxamido-bis(-diphenyltin)* (**4**)

An orange microcrystalline powder was obtained (98%) by a procedure analogous to **3**. It was recrys-

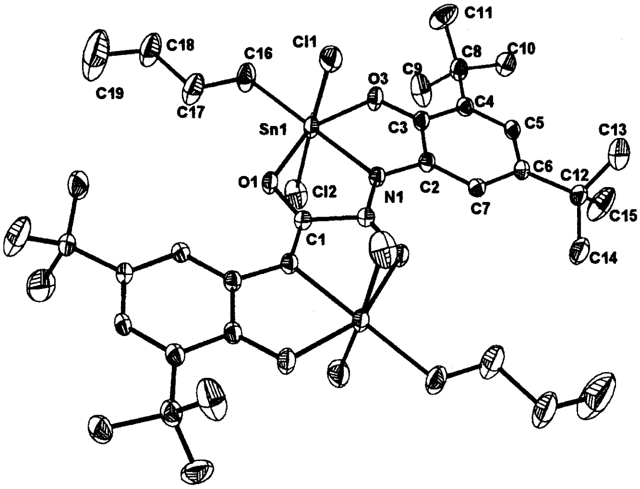


Fig. 10. Molecular structure of the dianion of compound **5**.

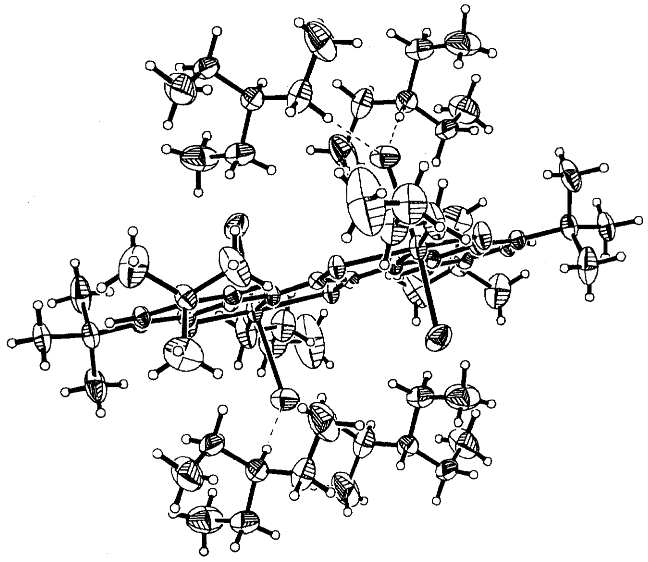


Fig. 11. View of the molecular structure of compound **5**, showing the intermolecular interactions between the chlorine atom and protons of the triethylammonium.

tallized from $CHCl_3$, orange crystals. M.p. 366–368°C. MS; (FAB+) *m*/*z* [M^+] 1038. IR (KBr) ν(cm^{-1}): 1600, 1470, 1434, 1410, 1364, 1290. Anal. Found: C, 61.03; H, 5.43; N, 2.75. Calc. for $C_{54}H_{60}N_2O_4Sn_2 \cdot 1/4CHCl_3$: C, 60.99; H, 5.68; N, 2.62%.

3.3.3. *Bis-(triethylammonium)-bis-(3,5-di-tert-butyl-2-oxo-phenyl)-oxamido-bis-(dichlorobutylstannate)* (*5*)

An orange crystalline powder was obtained (82%). It was recrystallyzed from ethylacetate. M.p. 270–272°C. MS; (EI) *m*/*z* 793. IR (KBr) ν(cm^{-1}): 3450 (N–H), 1618, 1474, 1398, 1362, 1268. Anal. Found: C, 50.04; H, 7.29; N, 4.82. Calc. for $C_{50}H_{90}N_4O_4Cl_4Sn_2$: C, 50.44; H, 7.61; N, 4.70%.

3.3.4. *Bis[(O–Sn)-ethanol]-bis(3,5-di-tert-butyl-2-oxo-phenyl)-oxamido-bis-(chlorophenyltin)* (*6*)

An orange crystalline powder was obtained (72%). It was recrystallyzed from ethanol–ethylacetate. M.p. 368–370°C. MS; (FAB+) *m*/*z* [M^+] 1038. IR (KBr) ν(cm^{-1}): 3478 (O–H), 1623, 1473, 1402, 1346. Anal. Found: C, 51.76; H, 6.18; N, 2.63. Calc. for $C_{46}H_{62}N_2O_6Cl_2Sn_2 \cdot H_2O$: C, 51.80; H, 6.05; N, 2.63%.

4. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre: Compound **1**, CCDC no. 147409; Compound **2a**, CCDC no. 148140; Compound **3**, CCDC no. 148141; Compound **4**, CCDC no. 148139; Compound **5**, CCDC no. 147407; and Compound **6**, CCDC no. 147408. Copies of the information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

Financial support from Conacyt-Mexico and Cinvestav is acknowledged as well as Conacyt-Mexico scholarships for M.G.-R. and V.M.J.-P. We thank M.A. Leiva-Ramírez for performing the X-ray diffraction studies of compound **1**.

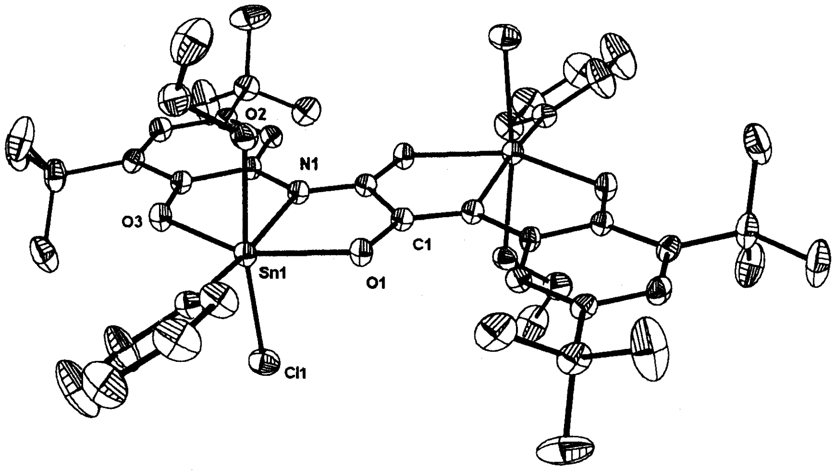


Fig. 12. Molecular structure of compound **6**.

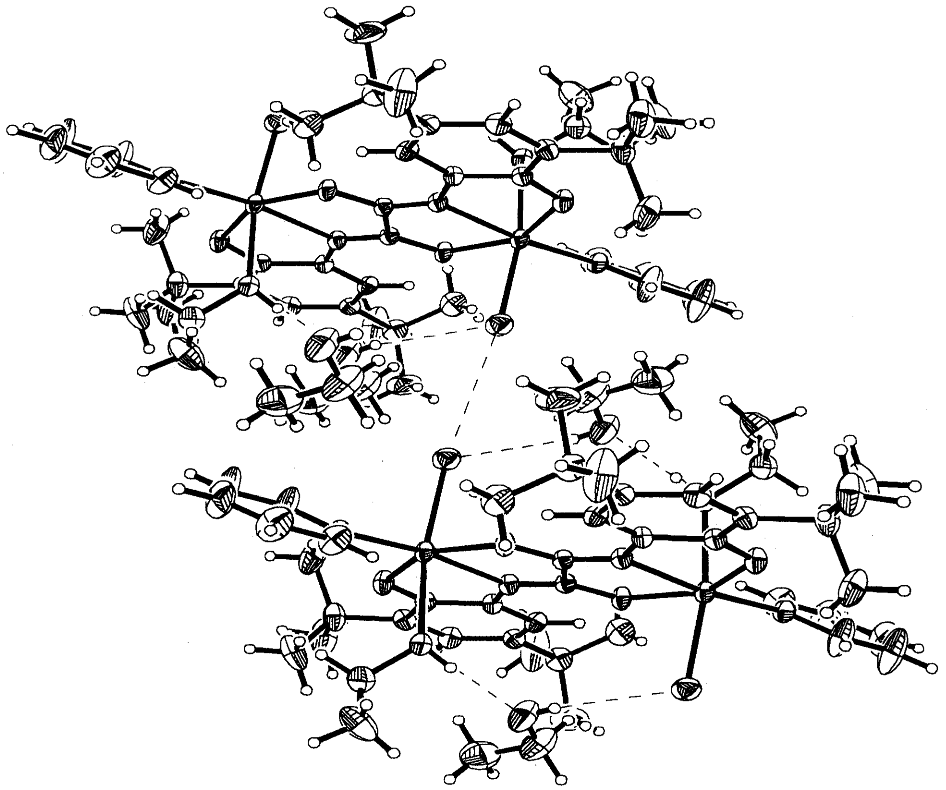


Fig. 13. Compound **6**, view of the intermolecular contacts between the chlorine atoms and the OH protons of ethanol of the lattice and between the OH proton of the coordinated ethanol and the oxygen of the ethanol of the lattice.

Table 6
Selected bond angles (°) of compounds **2**–**6**

	2	**3**	**4**	**5**	**6**
O1–Sn–O3		150.3(8)	151.4(3)	153.5(1)	153.4(1)
O1–Sn–N		74,4(1)	75.2(3)	75.8(1)	76.3(1)
O1–Sn–X				85.0(1) (Cl1)	81.6(1) (O2)
O1–Sn–Cl2				88.2(1)	92.0(1)
O1–Sn–C		93.9(1) (C16)	94.4(4) (C16)	99.5(1)	101.4(2)
O1–Sn–C		91.0(1) (C20)	89.4(4) (C22)		
O1–C1–C1A	120.6(1)	118.2(4)	119.3(1)	118.1(4)	118.5(5)
O3–Sn–N		77.2(1)	77.4(3)	77.8(1)	78.4(1)
O3–Sn–X				91.2(1) (Cl1)	87.0(2) (O2)
O3–Sn–Cl2				93.1(1)	96.3(1)
O3–Sn–C		102.8(1) (C16)	102.4(4) (C16)	106.6(1)	102.2(2)
O3–Sn–C		97.0(1) (C20)	97.2(4) (C22)		
C–Sn–C		128.9(1)	129.7(4)		
C1–N–C2	128.7(1)	127.3(3)	128.6(9)	129.0(3)	130.3(4)
N–Sn–C		107.2(1)(C16)	110.2(4) (C16)	172.0(2)	170.5(2)
N–Sn–C		123.0(1)(C20)	119.1(4) (C22)		
N–Sn–X				84.3(1) (Cl1)	82.0(2) (O2)
N–Sn–Cl				90.3(1) (Cl2)	90.6(1) (Cl1)
N–C1A–C1	112.8(1)	113.5(4)	112.9(1)	114.0(4)	113.3(5)
C–Sn–X				88.9(2) (Cl1)	88.5(2) (O2
C–Sn–Cl				96.0(2) (Cl2)	98.7(Cl1)
X–Sn–Cl				172.3(1) (Cl)	171.2(1) (O2)

Table 7
Crystal and data collection parameters

Compound	**1**	**2**	**3**	**4**	**5**	**6**
Empirical formula	$C_{28}H_{46}N_2O_2$	$C_{30}H_{44}N_2O_4$	$C_{46}H_{76}N_2O_4Sn_2$	$C_{56}H_{62}Cl_6N_2O_4Sn_2$	$C_{50}H_{90}Cl_4N_4O_4Sn_2$	$C_{50}H_{74}Cl_2N_2O_8Sn_2$
Formula weight	442.67	496.67	958.47	1277.16	1190.45	1146.8
Crystal size (mm)	0.09 × 0.10 × 0.12	0.2 × 0.24 × 0.44	0.1 × 0.1 × 0.5	0.25 × 0.28 × 0.42	0.14 × 0.28 × 0.50	0.31 × 0.62 × 0.64
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	$C2/c$	$P\bar{1}$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P\bar{1}$
a (Å)	19.4635(10)	8.0534(8)	7.8851(7)	9.2465(8)	9.628(2)	9.775(2)
b (Å)	6.2665(10)	9.4565(10)	18.1611(19)	29.939(2)	19.745(4)	11.182(2)
c (Å)	21.6534(10)	10.2581(11)	17.4155(19)	10.7897(10)	16.110(3)	14.814(3)
α (°)	90.00	87.060(2)	90.00	90.00	90.00	99.22(3)
β (°)	91.78	79.687(2)	102.334(2)	101.7692(1	97.55(3)	107.95(3)
γ (°)	90.00	69.868(2)	90.00	90.00	90.00	110.49(3)
V (Å^3)	2639.8(5)	721.60(13)	2436.4(4)	2924.1(4)	3036.0(10)	1376.1(5)
Z	4	1	2	2	2	1
ρ_{calc} (mg m^{-3})	1.114	1.143	1.307	1.451	1.302	1.375
μ (mm^{-1})	0.069	0.075	1.064	1.172	1.039	1.053
$F(000)$	976	270	996	1292	1236	586
Index range	$-22 \leq h \leq 22$ $-7 \leq k \leq 0$ $-25 \leq l \leq 0$	$-6 \leq h \leq 10$ $-12 \leq k \leq 12$ $-13 \leq l \leq 13$	$-5 \leq h \leq 5$ $-22 \leq k \leq 22$ $-21 \leq l \leq 21$	$-11 \leq h \leq 11$ $-38 \leq k \leq 33$ $-13 \leq l \leq 13$	$-11 \leq h \leq 11$ $0 \leq k \leq 24$ $0 \leq l \leq 19$	$-11 \leq h \leq 12$ $-13 \leq k \leq 0$ $-18 \leq l \leq 18$
2θ (°)	49.26	58.42	55.10	46.52	51.94	51.94
Temperature (K)	293(2)	193(2)	193(2)	193(2)	293(2)	293(2)
Reflections collected	2292	4231	13181	12820	5129	5666
Reflections unique	2225	2256	3493	3998	5129	5376
Reflections Observed (4σ)	845	1717	2543	3524	3522	4132
R_{int}	0.1241	0.0197	0.0592	0.0379	0.0000	0.0337
Variables	145	165	272	315	299	299
Weighting scheme [a] x/y	0.1330/0	0.0724/0	0.0275/0.0354	0.0951/39.7388	0.0571/0	0.0784/1.7227
Goodness-of-fit	0.958	1.068	1.001	1.198	0.979	1.086
Final R indicies (4σ)	0.0780	0.0387	0.0243	0.0767	0.0366	0.0417
Final wR_2	0.1939	0.1079	0.0522	0.1753	0.0953	0.1118
Largest res. peak (e Å^{-3})	0.243	0.170	0.456	3.318	0.507	1.330

[a] $w^{-1} = \sigma^2 F_o^2 + (xP)^2 + yP$; $P = (F_o^2 + 2F_c^2)/3$.

References

[1] R. Contreras, A. Murillo, G. Uribe, A. Klaebe, Heterocycles 23 (1985) 2187.

[2] M.A. Paz-Sandoval, C. Fernández-Vincent, G. Uribe, R. Contreras, A. Klaébé, Polyhedron 7 (1988) 679.

[3] N. Farfán, P. Joseph-Nathan, L.M. Chiquete, R. Contreras, J. Organometal. Chem. 348 (1988) 149.

[4] R. Contreras, A. Murillo, P. Joseph-Nathan, Phosphorus, Sulfur and Silicon 47 (1990) 215.

[5] A. Murillo, L.M. Chiquete, P. Joseph-Nathan, R. Contreras, Phosphorus, Sulfur Silicon 53 (1990) 87.

[6] C. Camacho-Camacho, F.J. Martínez-Martínez, M.J. Rosales-Hoz, R. Contreras, Phosphorus, Sulfur Silicon 91 (1994) 189.

[7] C. Camacho-Camacho, H. Tlahuext, H. Nöth, R. Contreras, Heteroatom. Chem. 9 (1997) 321.

[8] C. Camacho-Camacho, G. Merino, F.J. Martínez-Martínez, H. Nöth, R. Contreras, Eur. J. Inorg. Chem. (1999) 1021.

[9] A.Y. Girgis, A.L. Balch, Inorg. Chem. 14 (1975) 2724.

[10] C.G. Pierpont, S.K. Larsen, S.R. Boone, Pure Appl. Chem. (1988) 1331.

[11] S.K. Larsen, C.G. Pierpont, J. Am. Chem. Soc. 110 (1988) 1827.

[12] C.L. Simpson, S.R. Boone, C.G. Pierpont, Inorg. Chem. 35 (1996) 3519.

[13] A. Caneschi, A. Dei, D. Gatteschi, J. Chem. Soc. Chem. Commun. (1992) 630.

[14] S. Bruni, A. Caneshi, F. Cariati, C. Delfs, A. Dei, D. Gatteschi, J. Am. Chem. Soc. 116 (1994) 1388.

[15] G. Speier, J. Csihony, A.M. Whalen, C.G. Pierpont, Inorg. Chem. 35 (1996) 3519.

[16] G. Swarnabala, M.V. Rajasekharan, S. Padhye, Chem. Phys. Lett. 267 (1997) 539.

[17] D. Ruiz-Molina, J. Veciana, K. Wurst, D.N. Hendrickson, C. Rovira, Inorg. Chem. 39 (2000) 617.

[18] D.A. Lewis, D.J. Williams, A.M. Slawin, J.D. Woolins, Polyhedron 15 (1996) 555.

[19] B. Wrackmeyer, H.E. Maisel, W. Milius, Main Group Met. Chem. 20 (1997) 231.

[20] B.R. MacGarvey, A. Ozarowsky, Z. Tian, D.G. Tuck, Can. J. Chem. 73 (1995) 1213.

[21] M. Sabanero, E. Rojas, V. Torres, N. Farfán, A. Flores, R. Contreras, Microbios 82 (1995) 173.

[22] B.H. Keppler, Metal Complexes in Cancer Chemotherapy, VCH, Weinheim, 1993.

[23] M. Gielen, Tin Based Anti-tumor Drugs, Springer-Verlag, Berlin, 1990.

[24] V.L. Narayanan, M. Nasr, K.O. Paull, Tin Based Antitumour Drugs, NATO ASI Series, Springer, Berlin, 200–217 (1990) 69.

[25] A.G. Davies, P.J. Smith, in: G. Wilkinson (Ed.), Comprehensive Organometallic Chemistry, Pergamon Press, New York, 1982, p. 519.

[26] V.B. Vol'eva, T.I. Prokof'eva, A.I. Prokof'ev, I.S. Belostotskaya, N.L. Komissarova, V.V. Ershov, Russ. Chem. Bull. 44 (1995) 1720.

[27] V.N. Komissarov, L.Y. Ukhin, L.V. Vetoshkina, J. Org. Chem. USSR 26 (1990) 1888.

[28] F.J. Martínez-Martínez, A. Ariza-Castolo, H. Tlahuext, M. Tlahuextl, R. Contreras, J. Chem. Soc. Perkin Trans. 2 (1993) 1481.

[29] F.J. Martínez-Martínez, I.I. Padilla-Martínez, M.A. Brito, E.D. Geniz, R.C. Rojas, J.B.R. Saavedra, H. Höpfl, M. Tlahuextl, R. Contreras, J. Chem. Soc. Perkin Trans. 2 (1998) 401.

[30] B. Wrackmeyer, Annu. Rep. NMR Spectrosc. 16 (1985) 73.

[31] B. Wrackmeyer, Annu. Rep. NMR Spectrosc. 38 (1999) 201.

[32] R. Contreras, V.M. Jimenez-Pérez, C. Camacho-Camacho, M. Güizado-Rodríguez, B. Wrackmeyer, J. Organometallic Chem. 604 (2000) 229.