

Synthesis and crystal structure characterization of a novel eighteen-tin-nuclear macrocyclic complex

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Received 17th June 2003, Accepted 24th June 2003

First published as an Advance Article on the web 27th June 2003

The reaction of sodium salt dihydrate of 2-mercaptopyridine with di-*n*-butyltin dichloride in benzene affords a novel eighteen-tin-nuclear macrocyclic complex **1**, which is a highly centrosymmetric 48-member macrocycle containing two centrosymmetric ladders of hydrolysis.

Recently developments in coordination chemistry have produced numerous macrocyclic complexes through appropriate coordination geometry of organometal complexes and certain organic ligands.^{1–9} Among them organotin macrocycles are attracting more and more attention for their potential industrial applications and biological activities.¹⁰ As shown in these metallo-macrocyclic systems, ligands with multi-coordination or donor atoms and particular stereochemistry may lead to different specific architectures. Especially those carboxylate or mercapto ligands with additional donor atoms, such as a nitrogen atom, available for coordination to Sn, have been revealed to help the construction of interesting macrocyclic topologies.⁵ In our previous work, we have reported a novel penta-tin-nuclear macrocycle with heterocyclic sulfur and nitrogen donor ligands.¹¹ To continue our research on organotin(IV) complexes, we choose another fascinating ligand: 2-mercaptopyridine acid.

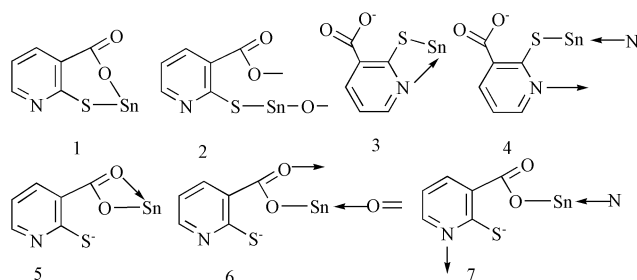
This ligand is interesting because of its potential multiple bidentate coordinate possibilities. As exhibited in Scheme 1, at least seven bonding modes between this ligand and tin are conceivable although nobody has investigated its actual coordination mode until now. However, its analogical ligands, such as mercaptopyridine and nicotinic acid systems which commonly possess a coordination atom and additional donor atom, have been extensively studied before.^{12–15} For example, organotin complexes with chelation by both S and O atoms (mode 1, 2) have been reported by Ng and Das, the ligand they chose is 2-mercaptobenzoic acid.¹⁶ The ligands 2-mercaptopyridine,^{14,17} 2-mercaptobenzothiazole,^{18,19} 2-mercaptopyrimidine¹⁵ and their derivatives are involved in S, N chelation to tin (mode 3), and their organotin derivatives have been characterized. O, O chelations (mode 5 and mode 6) are commonly observed in organotin carboxylates.^{12,20} In addition, bridging between different molecules *via* the heterocycles (mode 4, 6 and 7) rather than chelation is possible.⁵

The above considerations stirred our interest in some detail syntheses, structure patterns for diorganotin derivatives of the ligand. To our surprise, we obtained an unusual macro-

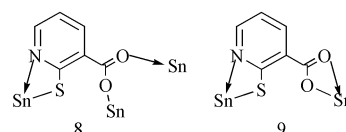
cyclic complex **1** by the reaction of sodium salt dihydrate of 2-mercaptopyridine with di-*n*-butyltin dichloride due to unexpected hydrolysis of di-*n*-butyltin dichloride. Complex **1** is a highly centrosymmetric 48-member macrocycle containing 18 tin nuclear. By a search of CSD, we found that only a few macrocyclic organotin complexes have been studied before,^{8,9} among which the largest one is a 24-member macrocycle containing 6 tin nuclear.⁸ So complex **1** can be regarded as the largest organotin macrocycle to date. Moreover, what is novel about **1** is that there exist two four-fold ladders of hydrolysis in its macrocycle. It is worthwhile noting that such structures appearing centrosymmetrically in a macrocycle is rare, although tetraorganodietannoxanes of the types [R₂(X)SnOSn(X)R₂]₂ and [R₂(OH)SnOSn(X)R₂]₂ (R = alkyl, Ph, Bu; X = halide, OR, OAc) have been extensively studied.^{21–25} The partial hydrolysis of di-*n*-butyltin dichloride may be attributed to the existence of H₂O molecules in our ligand. This present Communication deals with the special crystal structure and solution properties of **1**. †

The ¹¹⁹Sn NMR spectrum of complex **1** shows five distinct resonances at –121.2, –209.7, –210.8, –221.2 and –259.6, respectively. It is difficult to assign coordination with certainty to the tin atoms on the basis of these data. As reported in the literature,²⁶ values of δ (¹¹⁹Sn) in the ranges –210 to –400, –90 to –190 and 200 to –60 ppm have been associated with six-, five- and four-coordinate tin centers, respectively. On this basis we can only conclude roughly that there exist three five-coordinate and two six-coordinate tin centers in solution for complex **1**. In order to determine the fine structural details for **1**, a single crystal X-ray diffraction study was performed (the molecular structure of complex **1** is shown in Fig. 1: (a) each tin possesses two pendent *n*-butyl groups, however, for the purpose of clarity these have been omitted. (b) All *n*-butyl groups have been added but only a half of the non-H atoms are numbered because of their centrosymmetry).

As Fig. 1 showed, the structure of **1** is so complicated that there exist five distinct tin environments and two kinds of multi-coordination mode for ligands chelated to tin (Scheme 2). There are eight tin nuclei coordinated with ligands by mode 8 or mode 9 alternatively, that is, a half of them are linked with adjacent two ligands by O, O chelations (Sn(1), Sn(1A), Sn(3), and Sn(3A)) and the left by S, N chelations (Sn(2), Sn(2A), Sn(4), and Sn(4A)). For clarity, here we label those {O, O} chelated-tin as Sort I and those {S, N} chelated-tin as Sort II. The two sorts of tin atoms are both six-coordinate and appear at the macrocycle alternately. Together with the eight chelating ligands, they construct the basic framework of the 48-member macrocycle of **1**. Besides these cyclic-tin nuclei, there are ten endocyclic tin nuclei which are located within two four-fold ladders of



Scheme 1



Scheme 2

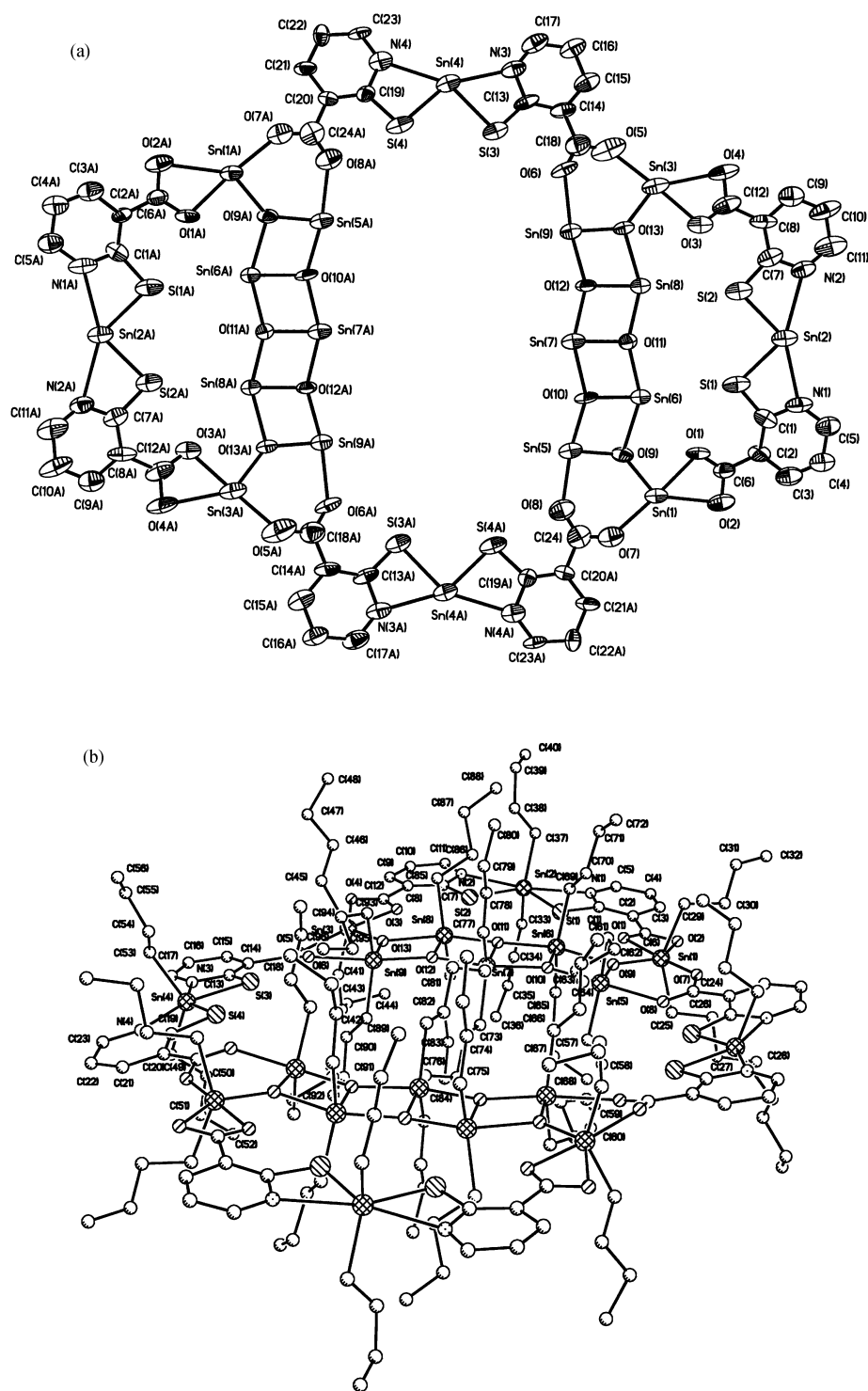


Fig. 1 (a) Molecular structure of **1** (omitting n-butyl groups), (b) molecular structure of **1** (only a half of the non-H atoms are numbered because of their centrosymmetry). Selected bond lengths (Å) and angles (°) for **1**: **Sn(1)**: Sn(1)–C(25) 2.113 (14), Sn(1)–C(29) 2.132 (16), Sn(1)–O(1) 2.237 (9), Sn(1)–O(2) 2.612 (10), Sn(1)–O(7) 2.314 (10), Sn(1)–O(9) 2.042 (7), O(1)–Sn(1)–O(2) 52.8 (3), O(9)–Sn(1)–O(1) 85.2 (3), O(7)–Sn(1)–O(2) 132.7 (3), O(9)–Sn(1)–O(7) 89.7 (3), C(25)–Sn(1)–C(29) 143.4 (6); **Sn(2)**: Sn(2)–C(33) 2.091 (17), Sn(2)–C(37) 2.147 (18), Sn(2)–S(1) 2.507 (4), Sn(2)–S(2) 2.501 (4), Sn(2)–N(1) 2.585 (11), Sn(2)–N(2) 2.666 (13), S(1)–Sn(2)–N(1) 59.3 (3), S(2)–Sn(2)–S(1) 89.08 (13), S(2)–Sn(2)–N(2) 59.7 (3), N(1)–Sn(2)–N(2) 151.9 (5), C(33)–Sn(2)–C(37) 130.8 (7); **Sn(3)**: Sn(3)–C(41) 2.227 (17), Sn(3)–C(45) 2.097 (14), Sn(3)–O(3) 2.218 (8), Sn(3)–O(5) 2.269 (12), Sn(3)–O(4) 2.655 (10), Sn(3)–O(13) 2.037 (7), O(3)–Sn(3)–O(4) 52.8 (3), O(5)–Sn(3)–O(4) 129.3 (4), O(13)–Sn(3)–O(3) 85.8 (3), O(13)–Sn(3)–O(5) 92.2 (4), C(45)–Sn(3)–C(41) 141.6 (9); **Sn(4)**: Sn(4)–C(49) 2.118 (14), Sn(4)–C(53) 2.126 (15), Sn(4)–S(3) 2.510 (4), Sn(4)–S(4) 2.506 (4), Sn(4)–N(3) 2.589 (12), Sn(4)–N(4) 2.628 (11), S(4)–Sn(4)–S(3) 91.52 (13), S(4)–Sn(4)–N(4) 60.4 (3), S(3)–Sn(4)–N(3) 60.2 (3), N(3)–Sn(4)–N(4) 147.8 (4), C(49)–Sn(4)–C(53) 128.6 (8); **Sn(5)**: Sn(5)–O(9) 1.993 (7), Sn(5)–C(57) 2.04 (2), Sn(5)–O(10) 2.078 (7), Sn(5)–C(61) 2.096 (15), Sn(5)–O(8) 2.290 (10), O(9)–Sn(5)–C(57) 117.0 (6), O(9)–Sn(5)–C(61) 113.8 (5), C(57)–Sn(5)–C(61) 128.9 (7), O(10)–Sn(5)–O(8) 170.0 (3); **Sn(6)**: Sn(6)–O(10) 2.056 (8), Sn(6)–Sn(7) 3.2910 (16), Sn(6)–O(11) 2.145 (7), Sn(6)–C(69) 2.131 (15), Sn(6)–C(65) 2.128 (17), Sn(6)–O(9) 2.273 (7), O(10)–Sn(6)–C(65) 109.8 (5), C(69)–Sn(6)–C(65) 139.0 (6), O(10)–Sn(6)–C(69) 110.8 (5), O(11)–Sn(6)–O(9) 149.9 (3); **Sn(7)**: Sn(7)–C(77) 2.04 (2), Sn(7)–C(73) 2.109 (14), Sn(7)–O(12) 2.139 (7), Sn(7)–O(10) 2.159 (6), Sn(7)–Sn(8) 3.2702 (16), Sn(7)–O(11) 2.035 (8), C(77)–Sn(7)–O(11) 120.8 (6), O(11)–Sn(7)–C(73) 123.5 (5), C(77)–Sn(7)–C(73) 115.7 (7), O(12)–Sn(7)–O(10) 153.6 (3); **Sn(8)**: Sn(8)–C(85) 2.097 (13), Sn(8)–O(11) 2.140 (7), Sn(8)–O(13) 2.265 (7), Sn(8)–O(12) 2.048 (8), Sn(8)–C(81) 2.144 (13), C(85)–Sn(8)–C(81) 137.8 (5), O(12)–Sn(8)–C(85) 109.3 (4), O(12)–Sn(8)–C(81) 111.8 (5), O(11)–Sn(8)–O(13) 151.0 (3); **Sn(9)**: Sn(9)–O(13) 2.000 (7), Sn(9)–C(89) 2.110 (16), Sn(9)–O(12) 2.104 (7), Sn(9)–C(93) 2.104 (15), Sn(9)–O(6) 2.328 (9), O(13)–Sn(9)–C(89) 115.0 (5), O(13)–Sn(9)–C(93) 111.2 (5), C(89)–Sn(9)–C(93) 133.1 (6), O(12)–Sn(9)–O(6) 170.4 (3).

hydrolysis. According to their different environment, we can divide them into another three sorts. The four tin atoms (Sn(5), Sn(5A) Sn(9) and Sn(9A)) that connect with the main framework of the macrocycle by one carboxyl oxygen atom of adjacent ligands are regarded as Sort III. The other four tin nuclei (Sn(6), Sn(6A) Sn(8) and Sn(8A)) and the two tin nuclei (Sn(7) and Sn(7A)) belong to Sort IV and Sort V, respectively. The following are some detailed studies on the five sorts of tin nuclei.

Sort I (Sn(1), Sn(1A), Sn(3), and Sn(3A)): Take Sn(1) for example. The tin atom in this case exists in a skew-trapezoidal planar geometry in which the basal plane is defined by four O atoms, two of which are derived from the carboxyl of the chelating ligand (O(1), O(2)), one from the second chelating ligand (O(7)) and the fourth from the ladder of hydrolysis (O(9)). The two remaining positions are occupied by the *n*-butyl groups (C(25) and C(29)), which lie over the weak Sn–O bonds (Sn(1)–O(2) and Sn(1)–O(7)). The carboxyl chelate the Sn center with asymmetric distances (Sn(1)–O(1), 2.237 (9) and Sn(1)–O(2), 2.610 (10)), as expected, the longer C–O bond distances are associated with the shorter Sn–O bonds. The degree of asymmetry between the two Sn–O bond distances is 0.373 Å.

Sort II (Sn(2), Sn(2A), Sn(4), and Sn(4A)): The four tin nuclei are all located on one of the C_2 axis of the macrocycle. Take Sn(2) for example. The tin atom connects with adjacent ligands by two sulfur and two nitrogen atoms, the same coordination as mode 3. In this case, two carbons and two sulfur atoms are covalently linked to the metal (C(33), C(37), S(1) and S(2)). The valence extension is performed *via* the nitrogen atoms of two ligand molecules (N(1) and N(2)). The Sn–N bond distances (Sn(2)–N(1), 2.585 (11) and Sn(2)–N(2), 2.666 (13) Å) are totally in agreement with the valence extension of the tin atom and lie within the sum of their respective Van der Waals radii (3.67 Å). The two chelating nitrogens occupy *cis* positions, as it is the case for the sulfur bonding. The strongly distorted square bipyramid presents apical *n*-butyl groups bound to tin and equatorial bidentate groups with nearly equal sulfur–tin and nitrogen–tin bonds. The sum of angles between the tin atom and equatorial ligating atoms (*i.e.* two N and two S) is 360.0° for Sn(2), which indicates that these four atoms are in the same plane.

Sort III (Sn(5), Sn(5A) Sn(9) and Sn(9A)): Take Sn(5) for example. The geometry of the tin atom is *cis*- R_2SnO_3 trigonal bipyramid. Tin forms four primary bonds: two to the butyl groups, two to oxygen atoms derived from the ladder of hydrolysis (O(9), O(10)). In addition, there exists coordination interaction between tin and one oxygen atom derived from the carboxyl of the adjacent ligand (O(8)). The sum of angles between the tin atom and equatorial atoms is 359.7° so the atoms Sn(5), C(57), C(61) and O(9) are almost in the same plane. The axial–tin–axial angle (O(10)–Sn(5)–O(8)) is 170.0 (3), which suggest that the structure are near to a normal trigonal bipyramid.

Sort IV (Sn(6), Sn(6A), Sn(8) and Sn(8A)): Take Sn(6) for example. The geometry of the tin atom is distorted *cis*- R_2SnO_3 trigonal bipyramid, typical for the so-called ladder structure of those tetraorganodistannoxane.^{21–25} The tin atom, connected with three bridging O atoms located at the ladder of hydrolysis, is a part of the Sn_2O_2 moiety and in this case, each O atom connects with three tin atoms. As a result, these O atoms are tridentate. The sum of angles between the tin atom and equatorial ligating atoms (O(10), C(65) and C(69)) is 359.0°, which indicates that these three atoms are almost in the same plane. The axial–tin–axial angle, O(11)–Sn(6)–O(9), is 149.9 (3)°, largely deviating from 180°. The obvious distortion may be due to the rigid framework of the ladder.

Sort V (Sn(7) and Sn(7A)): The geometries of the tin atoms are also both distorted *cis*- R_2SnO_3 trigonal bipyramid and they are both located at one of the C_2 axes of the macrocycle.

Furthermore, there exist very weak interactions between the tin atoms of Sort IV and those of Sort V. The Sn(6) \cdots Sn(7) separation is 3.2910 (16) Å and Sn(7) \cdots Sn(8) is 3.2702 (16) Å, much longer than that reported in the literature.^{27,28} These interactions between adjacent Sn atoms are too long to result in a formal increase in coordination number for each Sn atom although they do influence the degree of distortion of the coordination polyhedron about each Sn atom. Thus, these tin atoms are best described as having trigonal bipyramidal geometries. The conclusion is well supported by the ¹¹⁹Sn NMR spectra. The axial–tin–axial angle (O(10)–Sn(7)–O(12)) is 153.6 (3)° and the sum of the angles between the tin atom and equatorial ligating atoms (O(11), C(73) and C(77)) is 360.0°.

We thank the National Natural Foundation, P. R. China (20271025), the Key Teachers Foundation from the State Education Ministry of China and the National Natural Foundation of Shandong Province, P. R. China for financial support of this work.

Notes and references

† The melting point was obtained with Kofler micro melting point apparatus and was uncorrected. ¹¹⁹Sn NMR spectra were recorded on a Bruker AMX-300 spectrometer operating at 111.9 MHz. The spectra were acquired at room temperature (298 K) unless otherwise specified. The chemical shifts were reported in ppm and were stated relative to neat tetramethyltin. Elemental analyses were performed with a PE-2400II apparatus.

Preparation of 1: The reaction was carried out under nitrogen atmosphere. The sodium salt dihydrate of 2-mercaptocotinic acid (0.235 g, 1 mmol) and di-*n*-butyltin dichloride (0.303 g, 1 mmol) was added to the solution of absolute benzene (30 ml) in a Schlenk flask, stirred for 12 h at 40 °C and then filtered. The filtrate was gradually removed by evaporation under vacuum until white solid product was obtained. The solid was then recrystallized from *n*-hexane. Block crystal complex was formed. Yield (pure product): 64%. Mp > 200 °C (dec.). Elemental Analysis: Found: C, 41.46; H, 6.08; N, 2.00; Calcd.: C, 41.32; H, 6.29; N, 2.01%. ¹¹⁹Sn NMR (CDCl₃): –121.2, –209.7, –210.8, –221.2 and –259.6.

Crystal data for 1: C₁₉₂H₃₄₈N₅O₂₆S₆Sn₁₈, $M = 5577.68$, monoclinic, space group $P2(1)/n$, $Z = 2$, $a = 19.470$ (7) Å, $b = 20.117$ (7) Å, $c = 32.954$ (12) Å, $V = 12875$ (8) Å³, $a = \gamma = 90^\circ$, $\beta = 94.061$ (7)°, $\mu(\text{Mo } K\alpha) = 1.828$ mm^{–1}, $F(000) = 724$. GoF = 1.01, $D_c = 1.439$ g cm^{–3}. All X-ray crystallographic data were collected on a Bruker SMART CCD 1000 diffractometer. The structure was solved by direct methods and refined by a full-matrix least squares procedure based on F^2 using the SHELXL-97 program system. All data were collected at 298(2) K using graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) and corrected for Lorentz and polarization effects but not for absorption. All non-H atoms were included in the model at their calculated positions. The positions of hydrogen atoms were calculated, and their contributions in structural factor calculations were included. 73853 reflections collected ($\theta = 2.07^\circ$ to 26.37°) to give all the data for $R_1 = 0.3465$ and $wR_2 = 0.1120$, 26068 of which were used in the refinement to give the final $R_1 = 0.0545$ and $wR_2 = 0.0711$ [$I > 2\sigma(I)$]. Residual electron density: 0.628 and -0.409 e Å^{–3}. It should be noted that the data for 1 are not satisfactory enough due to complications concerning the vibration parameter of many atoms and a low percent of reflections, which may result from the poor quality of the crystal. Further improvement of the data is underway and expected to be reported in a full paper. CCDC reference number 204621. See <http://www.rsc.org/suppdata/dt/b3/b306932j/> for crystallographic data in CIF or other electronic format.

- 1 M. Eshel and A. Bino, *Inorg. Chim. Acta.*, 2001, **320**, 127.
- 2 O. I. Shchegolikhina, V. A. Igonin, Yu. A. Molodtsova, Yu. A. Pozdniakova, A. A. Zhdanov, T. V. Strelkova and S. V. Lindeman, *J. Organomet. Chem.*, 1998, **562**, 141.
- 3 E. Kiss, K. Petrohan, D. Sanna, E. Garrirba, G. Micera and T. Kiss, *Polyhedron*, 2000, **19**, 55.
- 4 D. Dakternieks, A. Duthie and B. Zobel, *Organometallics*, 2002, **21**, 647.
- 5 S. Bhandari, M. F. Mahon, J. G. McGinley, K. C. Molloy and C. E. E. Roper, *J. Chem. Soc., Dalton Trans.*, 1998, 3425.
- 6 M. Verdenelli, S. Parola, L. G. Hubert-Pfalzgraf and S. Lecocq, *Polyhedron*, 2000, **19**, 2069.
- 7 P. B. Hitchcock, M. F. Lappert, G. A. Lawless, G. M. de Lima and L. J.-M. Piersseas, *J. Organomet. Chem.*, 2000, **601**, 142.

- 8 T. P. Lockhart, *Organometallics*, 1988, **7**, 1438.
- 9 Ok-Sang Tung, Y. S. Sohn and J. A. Ibers, *Inorg. Chem.*, 1986, **25**, 2273.
- 10 S. K. Duboy and U. Roy, *Appl. Organomet. Chem.*, 2003, **17**, 3.
- 11 C. L. Ma, F. L., D. Q. Wang and H. D. Yin, *J. Organomet. Chem.*, 2003, **667**, 5.
- 12 M. Gielen, A. E. Khloufi, M. Biesemans and R. Willem, *Polyhedron*, 1992, **11**, 1861.
- 13 M. D. Couce, G. Faraglia, U. Russo and G. Valle, *J. Chem. Crystallogr.*, 1996, **26**, 479.
- 14 M. V. Castano, A. Macias, A. Castineiras, A. S. Gonzalez, E. G. Martinez, J. S. Casas, J. Sordo, W. Hiller and E. E. Castellano, *J. Chem. Soc., Dalton Trans.*, 1990, 1001.
- 15 R. Schmiedgen, F. Huber, Arturo Silvestri, G. Ruisi, M. Rossi and R. Barbieri, *Appl. Organomet. Chem.*, 1998, **12**, 861.
- 16 S. W. Ng and V. G. K. Das, *J. Crystallogr. Spectrosc. Res.*, 1993, **23**, 925.
- 17 M. Boualam, J. Meunier-PIRET, m. Biesemans, R. Willem and M. Gielen, *Inorg. Chim. Acta.*, 1992, **198–200**, 249.
- 18 S. K. Hadjikakou, M. A. Demertzis, M. Kubicki and D. Kovalas-Demertzi, *Appl. Organomet. Chem.*, 2000, **14**, 727.
- 19 J. Susperregui, M. Bayle, J. M. Leger and G. Deleris, *J. Organomet. Chem.*, 1998, **556**, 105.
- 20 S. G. Teoh, S. H. Ang, E. S. Looi, C. A. Keok, S. B. Teo and J. P. Declercq, *J. Organomet. Chem.*, 1996, **523**, 75.
- 21 C. L. Ma and F. L., *Chin. J. Chem.*, 2003, **21**, 146.
- 22 M. Gielen, H. Dalil, M. Biesemans, B. Mahieu, D. de Vos and R. Willem, *Appl. Organomet. Chem.*, 1999, **13**, 515.
- 23 J. S. Casas, A. Castineiras, F. Condori, M. D. Couce, U. Russo, A. Sanchez, J. Sordo and J. M. Varela, *Polyhedron*, 2000, **19**, 813.
- 24 F. Ribot, C. Sanchez, A. Meddour, M. Gielen, E. R. T. Tiekink, M. Biesemans and R. Willem, *J. Organomet. Chem.*, 1998, **552**, 177.
- 25 M. Kemmer, H. Dalil, M. Biesemans, J. C. Martins, B. Mahieu, E. Horn, D. de Vos, E. R. T. Tiekink, R. Willem and M. Gielen, *J. Organomet. Chem.*, 2000, **608**, 63.
- 26 J. Holecek, M. Nadvornik, K. Handlir and A. Lycka, *J. Organomet. Chem.*, 1986, **315**, 299.
- 27 M. J. Chetcuti, M. H. Chisholm, H. T. Chiu and J. C. Huffman, *J. Am. Chem. Soc.*, 1983, **105**, 1060.
- 28 S. Masamune and L. R. Sita, *J. Am. Chem. Soc.*, 1983, **105**, 630.