

The crystal structure of di-2-aminopyrimidinium tetraphenyldichloro(μ -oxo)distannate

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Abstract

Hydrolysis of diphenyltin dichloride in the presence of diethyl ether proceeds via formation of an ionic, monomeric diorganodistannoxane compound. The single-crystal X-ray diffraction study of $(C_4H_6N_3)_2[SnPh_2OCl]_2$ is reported, together with IR data. The dimer consists of five coordinate tin(IV) units with di- μ -oxo bridging. The coordination geometry of the tin unit is a distorted trigonal bipyramid with two phenyl groups and one μ -oxo in equatorial positions, and the other two μ -oxo and chlorine atoms in axial positions.

Keywords: Tin; 2-Aminopyrimidine; Stannoxane; Crystal structure; IR spectroscopy; X-ray diffraction; Hydrolysis

1. Introduction

Organotin complexes may interact with biological systems in many different ways, as, for instance, bactericides, fungicides, acaricides and industrial biocides [1]. In recent years, several investigations have been carried out [2] to test their antitumor activity, and it has been observed that several organotin complexes are effective antineoplastic (mainly antileukaemic) agents. The mechanism of their activity may involve the transportation of the complexed organotin compound into the tumor cells, followed by reaction of uncomplexed organotin and its hydrolysis product at the active sites. This suggestion is supported by the fact that the hydrolysis product is active [2d]. Hydrolysis of diorganotin and monoorganotin compounds, R_2SnCl_2 and $RSnCl_3$, results in the formation of four-membered cyclic distannoxane rings [3]. One distannoxane ring unit is present in the structure of dimethyltin nitrate hydroxide $[(CH_3)_2Sn(NO_3)OH]_2$ dimeric, through bridging hydroxyl groups with distorted trigonal-bipyramidal geometry [4], and in the dimeric structure of six-coordinated ethyldichlorotin oxide monohydrate $[C_2H_5SnCl_2OH(H_2O)]_2$ [5]. Three distannoxane rings are present in a class of dimeric tetraorganodistannoxanes of planar ladder arrangement with distorted trigonal-bipyramidal

geometry about the five-coordinated tin centers [3,6]. Six distannoxane ring units are present in the structural classes of organotin oxy carboxylates, which have "drum" and "open drum" or "ladder" structures [3,6]. Representation of organotin structures of one and three distannoxane units, based on X-ray determinations, are shown in Fig. 1.

As an extension of our research on tin compounds with heterocyclic derivatives of biological and pharmaceutical importance [7], we report here the synthesis and solid state X-ray characterization of $(C_4H_6N_3)_2[SnPh_2OCl]_2$. To our knowledge this derivative provides the first example of a five-coordinated anionic distannoxane.

2. Experimental

2-Aminopyrimidine ($C_4N_3H_6$) and diphenyltin dichloride (Ph_2SnCl_2) were used as received. Solvents were purified according to standard procedures.

2.1. Synthesis

Diphenyltin dichloride (0.34 g, 1 mmol) was dissolved in diethyl ether (25 ml), stirred and 2-aminopyrimidine (0.281 g, 3 mmol) was added to the above solution. The reaction mixture was stirred at room temperature for 24 h. The white solid that formed

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was washed with the same solvent (0.466 g, yield 55%). M.p. 132–134°C. Anal. Found: C, 43.34; H, 3.76; N, 10.76; Cl, 13.90. $(\text{SnPh}_2\text{Cl}_2)_2(\text{C}_4\text{N}_3\text{H}_5)_3(\text{H}_2\text{O})_2$, **1**. Calc.: C, 42.82; H, 3.87; N, 12.49; Cl, 14.06. **1** was recrystallized from a mixture of acetonitrile and methanol (1:1) at room temperature, resulting in the formation of $(\text{C}_4\text{H}_6\text{N}_3)_2[\text{SnPh}_2\text{OCl}]_2$, di-2-aminopyrimidinium tetraphenyldichloro(μ -oxo)distannate, **2**, M.p. 152–154°C. Anal. Found: C, 45.10; H, 3.40; N, 10.40; Cl, 9.00. **2**. Calc.: C, 45.61; H, 3.83; N, 9.98; Cl, 8.31%.

2.2. Crystal structure determination

A crystal suitable for X-ray diffraction (rectangular prism, $0.27 \times 0.35 \times 0.32$ mm) was mounted on an Enraf-Nonius CAD4 diffractometer using graphite-monochromatized Mo K α radiation ($\lambda = 0.71069$ Å). Unit cell parameters and orientation matrices were obtained from the setting angles of 25 reflections ($12 < \theta < 15^\circ$) and refined by least-squares. Data were measured at -50°C using an ω - 2θ motion. No significant decay was observed. Crystallographic data and other pertinent information are shown in Table 1. Data was normally corrected by Lorentz and polarization effects, but not for absorption. The position of the tin atom was found using SHELX-86 [8a] and all subsequent calculations were performed using CRYSTALS [8b]. Except for amino H atoms, that were refined using slack con-

straints [8c,d], the rest of the hydrogen atoms, although found, were positioned geometrically, their positions being recalculated after each refinement cycle. All non-hydrogen atoms were refined anisotropically. In the final stage of the refinement, an overall isotropic extinction parameter was introduced and a Chebychev weighting scheme was used with coefficients 2.57, 0.01 and 4.27 [8e]. Final refinement was continued until the maximum value of the shift/esd (estimated standard deviation) ratio was less than 0.01. Illustrations were drawn using ORTEP [8f].

Hydrogen 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

Diphenyltin dichloride reacts with 2-aminopyrimidine (1:3 molar ratio) to give **1**. The formation of the ionic substance **2** proceeds by recrystallization of **1** in $\text{CH}_3\text{CN}:\text{MeOH}$ solution at room temperature. A hydrolysis pathway yields the distannoxane ring.

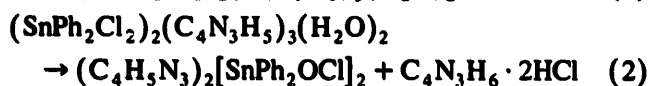
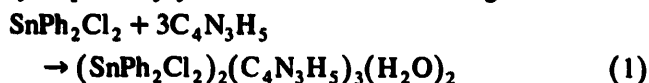
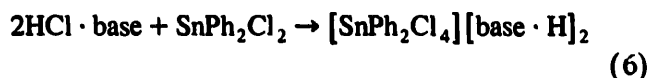
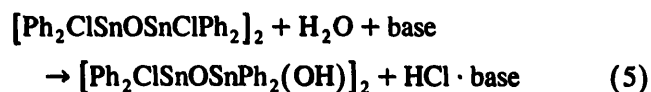
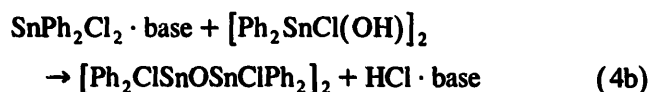
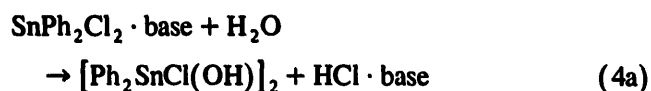
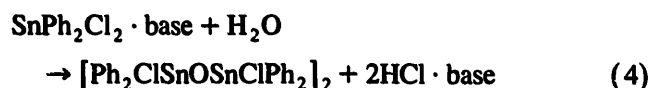


Table 1
Summary of crystal and intensity collection data for **2**

Formula	$\text{C}_{32}\text{H}_{32}\text{N}_6\text{Cl}_2\text{O}_2\text{Sn}_2$
<i>M</i>	840.93
Crystal size (mm ³)	$0.27 \times 0.35 \times 0.32$
Crystal system	Triclinic
Space group	$\text{P}\bar{1}$
<i>a</i> (Å)	9.262(1)
<i>b</i> (Å)	9.826(1)
<i>c</i> (Å)	10.553(1)
α (°)	62.60(1)
β (°)	86.13(2)
γ (°)	83.08(2)
<i>V</i> (Å ³)	846.4(4)
<i>Z</i>	1
<i>D_x</i> (Mg m ⁻³)	1.65
μ (cm ⁻¹)	16.77
Scan technique	ω - 2θ
Scan range (ω)	2.39–23.50
Maximum absorption correction factor	1.53
Reflections collected	2666
independent reflections	2491
Reflections observed	2110 reflected [$I \geq 3\sigma(I)$]
Index ranges	$0 \leq h \leq 10, -11 \leq k \leq 11, -11 \leq l \leq 11$
<i>F</i> (000)	416
$R = \sum(F_o - F_c) / \sum F_o $	0.0392
$w = 1/\sigma(F_o)$	
$R_w = [\sum_w(F_o - F_c)^2 / \sum_w F_o ^2]^{1/2}$	0.0372

Holmes and coworkers [3a] studied the base-catalyzed (base = quinuclidine, 1,4-diazobicyclo[2,2,2]octane, or acridine) hydrolysis of SnPh_2Cl_2 and a mechanistic sequence was proposed, leading to the formation of the hydroxydistannoxane (Eqs. (3)–(6)). The hydroxyhalide species $[\text{R}_2\text{SnX}(\text{OH})]_2$ was postulated as a precursor to the formation of the dihalodistannoxane $\text{R}_2\text{XSnOSnR}_2\text{X}$ although no evidence was found for the presence of this transient species, considered to be responsible for the lability of this class of substances.



In our case, the base reaction with SnPh_2Cl_2 stabilizes this transient species in the formation of the ionic substance. The molecular geometry of **2** and its atom-labeling scheme are shown in Fig. 2. Fractional atomic coordinates and bond lengths and angles are given in Tables 2 and 3. Thermal parameters, hydrogen atom parameters and additional bond lengths and angles are provided as supplementary material.

The structure consists of 2-aminopyrimidinium ($\text{C}_4\text{H}_6\text{N}_3$)⁺ cations and $[\text{Sn}_2\text{Ph}_4\text{Cl}_2\text{O}_2]^{2-}$ anions. The structure is centrosymmetric with the halves of the anionic dimer related by a crystallographic inversion center located in the center of the four-membered $(\text{SnO})_2$ ring. For the purposes of electrical neutrality, two cations are required for each binuclear tin species. The X-ray results showed two ($\text{C}_4\text{H}_6\text{N}_3$)⁺ cations for each binuclear species and gave indications of possible protonation of the nitrogen atom N(3) of the amino group with $\text{N}(3) \cdots \text{O}(1) > 3.01 \text{ \AA}$. The counterion 2-aminopyrimidine⁺ is planar, with maximum deviation 0.03(5) Å for C(16), and its plane is nearly perpendicular to the planes of the two phenyl rings (angle 92.6(4)° with the plane C(1)–C(6) and 90.1(4)° with the plane C(7)–C(12)).

In the anion, the geometry around each tin atom can be described as distorted trigonal-bipyramidal. The three nearest neighbors of the tin atom Sn(1) are the two carbon atoms C(1) and C(7) from the phenyl groups, at a distance $\text{Sn}(1)\text{--C}(1) = 2.120(3) \text{ \AA}$ and $\text{Sn}(1)\text{--C}(7) =$

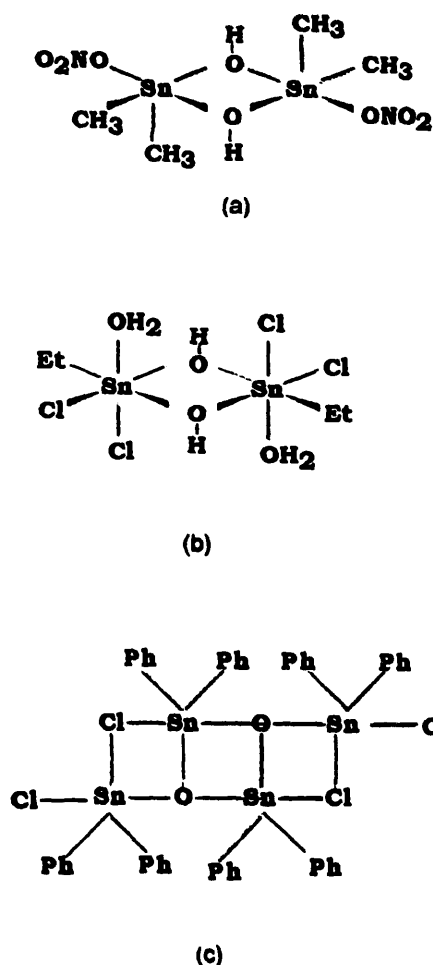


Fig. 1. The structure of (a) $[(\text{CH}_3)_2\text{Sn}(\text{NO}_3)\text{OH}]_2$, (b) $[\text{C}_2\text{H}_5\text{SnCl}_2\text{OH}(\text{H}_2\text{O})]_2$ and (c) dimeric tetraphenyldistannoxane.

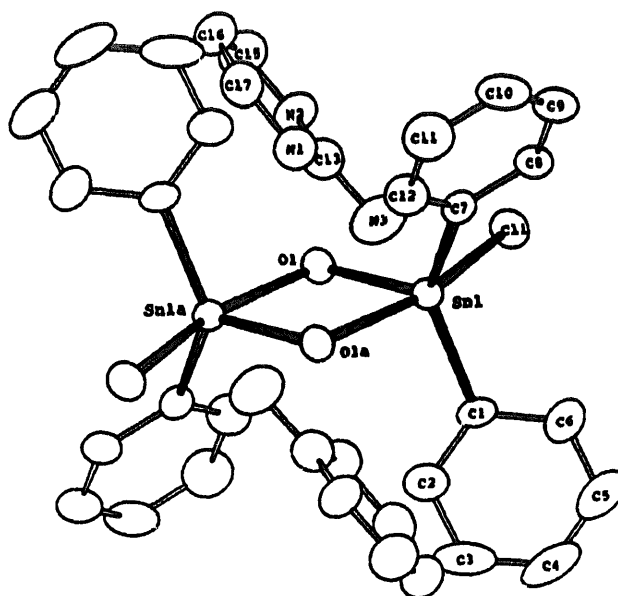


Fig. 2. The atom-labeling scheme of the dimer $(\text{C}_4\text{H}_6\text{N}_3)_2[\text{SnPh}_2\text{OCl}]_2$. All hydrogen atoms have been omitted.

Table 2
Fractional atomic coordinates and equivalent isotropic thermal parameters (\AA) for the non-hydrogen atoms of **2**

Atom	x	y	z	U_{iso}
Sn(1)	0.50157(3)	0.19481(3)	0.89489(3)	0.0263
Cl(1)	0.6237(1)	0.3207(1)	0.6601(1)	0.0356
O(1)	0.5680(3)	-0.0131(3)	0.9014(3)	0.0314
Cl(1)	0.6412(4)	0.2729(5)	0.9933(4)	0.0312
C(2)	0.7160(6)	0.1734(6)	1.1169(5)	0.0471
C(3)	0.8140(7)	0.2322(9)	1.1710(6)	0.0599
C(4)	0.8353(7)	0.3863(9)	1.1023(8)	0.0543
C(5)	0.7612(8)	0.4830(7)	0.9818(8)	0.0566
C(6)	0.6645(6)	0.4270(6)	0.9268(6)	0.0490
C(7)	0.2857(5)	0.2821(5)	0.8205(4)	0.0306
C(8)	0.2620(5)	0.4168(5)	0.6952(4)	0.0351
C(9)	0.1210(6)	0.4751(6)	0.6464(5)	0.0452
C(10)	0.0040(5)	0.3993(7)	0.7204(5)	0.0449
C(11)	0.0266(5)	0.2637(7)	0.8450(6)	0.0489
C(12)	0.1679(5)	0.2020(6)	0.8997(5)	0.0423
N(1)	0.6559(5)	-0.0765(5)	0.6764(4)	0.0455
C(13)	0.7859(5)	-0.0476(6)	0.6115(5)	0.0418
N(2)	0.8482(5)	-0.1098(6)	0.5256(5)	0.0522
C(14)	0.7679(7)	-0.1985(7)	0.5032(7)	0.0557
C(15)	0.6307(7)	-0.2275(7)	0.5568(6)	0.0566
C(16)	0.5781(6)	-0.1646(6)	0.6460(6)	0.0516
N(3)	0.8649(6)	0.0434(7)	0.6358(6)	0.0589

2.128(3) \AA , and one oxygen atom O(1) at a distance Sn(1)–O(1) = 2.032(3) \AA . The tin atom is also very close to this plane (plane I) at a distance of 0.12(5) \AA . The apical positions are occupied by the atoms Cl(1) and O(1a) at distances Sn(1)–Cl(1) = 2.467(1) \AA and Sn(1)–O(1a) = 2.187(3) \AA . The bridging oxygen atoms O(1) and O(1a) form a perfect plane (plane II) with the two metal atoms, due to symmetry. The angle between the planes I and II is 89.3(3) $^\circ$. The planes of the two phenyl groups form an angle 133.2(3) $^\circ$.

The IR spectrum shows one band at 380 cm^{-1} attributable to $\nu(\text{Sn}-\text{Cl})$, two bands at 450 and 440 cm^{-1} assignable to $\nu_{\text{as,s}}(\text{Sn}-\text{O})$ and two bands at 280 and 260 cm^{-1} assignable to $\nu_{\text{as,s}}(\text{Sn}-\text{C})$, indicating non-linear Sn–O₂ and Sn–C₂ moieties [7]. This arrangement is consistent with the X-ray diffraction study. The N–H stretching absorption region of the free ligand shows two sharp bands at 3350 and 3168 cm^{-1} , super-

Table 3
Selected bond distances (\AA) and bond angles ($^\circ$) for **2**

Sn(1)–Cl(1)	2.467(1)	O(1)–Sn(1)–Cl(1)	89.07(8)
Sn(1)–O(1)	2.032(3)	O(1)–Sn(1)–Cl(1a)	160.08(8)
Sn(1)–O(1a)	2.187(3)	O(1)–Sn(1)–O(1a)	71.2(1)
Sn(1)–Cl(1)	2.120(4)	C(1)–Sn(1)–Cl(1)	93.1(1)
Sn(1)–C(7)	2.128(4)	C(1)–Sn(1)–O(1)	115.7(1)
C(1)–C(2)	1.387(7)	C(1)–Sn(1)–O(1a)	93.2(1)
C(1)–C(6)	1.383(7)	C(7)–Sn(1)–Cl(1)	96.4(1)
C(2)–C(3)	1.408(8)	C(7)–Sn(1)–O(1)	114.0(1)
C(3)–C(4)	1.38(1)	C(7)–Sn(1)–O(1a)	94.1(1)
C(4)–C(5)	1.36(1)	C(7)–Sn(1)–C(1)	129.5(2)
C(5)–C(6)	1.387(9)	Sn(1)–O(1)–Sn(1a)	108.8(1)
C(7)–C(8)	1.381(6)	C(2)–C(1)–Sn(1)	122.2(3)
C(7)–C(12)	1.410(7)	C(6)–C(1)–Sn(1)	118.5(4)
C(8)–C(9)	1.392(7)	C(6)–C(1)–C(2)	119.1(4)
C(9)–C(10)	1.372(8)	C(3)–C(2)–C(1)	119.0(5)
C(10)–C(11)	1.380(8)	C(4)–C(3)–C(2)	120.6(6)
C(11)–C(12)	1.416(7)	C(5)–C(4)–C(3)	120.1(5)
C(13)–N(1)	1.339(7)	C(6)–C(5)–C(4)	120.1(6)
C(13)–N(2)	1.362(6)	C(5)–C(6)–C(1)	121.1(6)
C(13)–N(3)	1.340(7)	C(8)–C(7)–Sn(1)	119.8(3)
C(14)–C(15)	1.363(9)	C(12)–C(7)–Sn(1)	119.7(3)
C(14)–N(2)	1.325(8)	C(12)–C(7)–C(8)	120.5(4)
C(15)–C(16)	1.381(8)	C(9)–C(8)–C(7)	120.1(4)
C(16)–N(1)	1.345(7)	C(10)–C(9)–C(8)	120.9(5)
		C(11)–C(10)–C(9)	119.5(5)
		C(12)–C(11)–C(10)	121.4(5)
		C(11)–C(12)–C(7)	117.6(5)
		N(2)–C(13)–N(1)	124.9(5)
		N(3)–C(13)–N(1)	118.3(4)
		N(3)–C(13)–N(2)	116.7(5)
		N(2)–C(14)–C(15)	124.0(5)
		C(16)–C(15)–C(14)	116.3(6)
		N(1)–C(16)–C(15)	122.3(5)
		C(16)–N(1)–C(13)	116.5(4)
		C(14)–N(2)–C(13)	115.7(5)

imposed on a broad band centered at 3100 cm^{-1} . These relatively low frequencies may be due to intramolecular hydrogen bonding in the ligand. This pattern is not much different from that exhibited by the complex **2**, having two strong bands centered at 3420 and 3170 cm^{-1} , superimposed on a broad band at 3000 cm^{-1} . This slight shift may be due to the protonated NH_3^+ group [9], as evidenced by X-ray diffraction analysis.

Summarized in Table 4 is a comparison of bond

Table 4
Bond lengths and interbond angles for dimeric tin(IV) derivatives with distannoxane ring

Compound	Coordination number	Bond length		Angle		Ref.
		Sn–O	Sn–Cl	O–Sn–O	Sn–O–Sn	
[SnEt(OH(OH ₂)Cl ₂) ₂]	6	2.110(11)	2.423(8) av.	70.9(6)	109.1(7)	[4]
[SnBu(OH(OH ₂)Cl ₂) ₂]	6	2.047(4)	2.484(2)	69.6(2)	110.4(2)	[5b]
		2.169(4)	2.419(2)			
[Sn(C ₂ H ₄ O ₂) ₂ Cl ₂][H][Et ₄ N]	6	2.116(3) av.	2.451(2)	69.1(1) av.	110.2(2) av.	[5b]
(C ₃ H ₅ N ₂) ₂ [SnMe ₂ (NO ₃) ₂ (OH) ₂]	7	2.129(4)		74.7(1)	100.53(2)	[10]
		2.162(4)				
(C ₄ H ₆ N ₃) ₂ [SnPh ₂ OCl ₂]	5	2.032(3)	2.467(1)	71.2(1)	108.8(1)	This work
		2.187(3)				

parameters of related tin(IV) compounds that have the distannoxane ring system. The range of Sn–O bond lengths is narrow, 2.05–2.20 Å, coinciding with the single bond covalent radius value of 2.13 Å [6b,7], reflecting the strong coordination within the dimer, and consistent with similar bond lengths in other distannoxanes. The range of Sn–Cl bonds is also surprisingly narrow, 2.42–2.47 Å. The range of O–Sn–O and Sn–O–Sn bond angles, 70.9–74.7° and 105.3–110.4° respectively, are close to one another for all the distannoxanes. The Sn–C bonds to both tins (2.120(3) and 2.128(3) Å) are consistent with the values observed in other phenyltin derivatives [6] or the mean Sn–C distance in a variety of organotin compounds (2.18(3) Å) [11].

References

- [1] (a) J.J. Zuckerman (ed.), *Organotin Compounds: New Chemistry and Applications*, Adv. Chem. Ser., No. 157, Am. Chem. Soc., 1976. (b) C.J. Evans and S. Karpel, Organotin compounds in modern technology, *J. Organomet. Chem. Lib.*, 76 (1985) 1. (c) S.J. Blunden, P.A. Cusack and R. Hill, *Industrial Uses of Tin Chemicals*, Roy. Chem. Soc., London, 1985.
- [2] (a) P.J. Sadler, *Chem. Ber.*, 18 (1982) 182. (b) A.J. Crowe, in M. Gielen (ed.), *Metal-Based Antitumour Drugs*, Vol. 1, Freund, London, 1989, pp. 103–149. (c) I. Haiduc and C. Silvestru, *Organometallics in Cancer Chemotherapy*, Vol. 1, *Main Group Metal Compounds*, CRC, Boca Raton, FL, 1989. (d) A.K. Saxena and F. Huber, *J. Coord. Chem.*, 95 (1989) 109 and references cited therein.
- [3] (a) J.F. Vollano, R.O. Day and R.R. Holmes, *Organometallics*, 3 (1984) 745. (b) A.S. Mufti and R.C. Poller, *J. Chem. Soc.*, (1965) 5055.
- [4] A.M. Domingos and G.M. Sheldrick, *J. Chem. Soc., Dalton Trans.*, (1974) 475.
- [5] (a) C. Lecomte, C.L.J. Protas and M. Devaud, *Acta Crystallogr.*, B32 (1976) 923. (b) J.A. Zubieta and J.J. Zuckerman, *Progr. Inorg. Chem.*, 24 (1978) 251.
- [6] (a) V. Chandrasekhar, R.O. Day, J.M. Holmes and R.R. Holmes, *Inorg. Chem.*, 27 (1988) 958 and references cited therein. (b) R.R. Holmes, S. Shafieezad, V. Chandrasekhar, J.M. Holmes and R.O. Day, *J. Am. Chem. Soc.*, 110 (1988) 1174.
- [7] (a) P. Tauridou, U. Russo, G. Valle and D. Kovala-Demertzi, *J. Organomet. Chem.*, 44 (1993) C16. (b) D. Kovala-Demertzi, P. Tauridou, J.M. Tsangaris and A. Moukarika, *Main Group Met. Chem.*, 5 (16) (1993) 315. (c) P. Tauridou, U. Russo, D. Marton, G. Valle and D. Kovala-Demertzi, *Inorg. Chim. Acta*, 231 (1995) 139. (d) D. Kovala-Demertzi, P. Tauridou, A. Moukarika, J.M. Tsangaris, C.P. Raptopoulou and A. Terzis, *J. Chem. Soc., Dalton Trans.*, (1995) 123. (e) D. Kovala-Demertzi, P. Tauridou, U. Russo and M. Gielen, *Inorg. Chim. Acta*, in press.
- [8] (a) G.M. Sheldrick, *SHELXS-86 Program for the solution of crystal structures*, University of Göttingen, Germany, 1985. (b) D.J. Watkin, J.R. Carruthers and P.W. Betteridge, *CRYSTALS*, Chemical Crystallographic Laboratory, Oxford University, 1985. (c) J.T. Waser, *Acta Crystallogr.*, 16 (1963) 1091. (d) J.S. Rollet, in F.R. Ahmed (ed.), *Crystallographic computing*, Munksgaard, Copenhagen, 1969, p. 169. (e) J.R. Carruthers and D.J. Watkin, *Acta Crystallogr.*, A35 (1979) 698. (f) C.K. Johnson, *ORTEP II*, Rep. ORNL-5138, Oak Ridge National Laboratory, TN, 1976.
- [9] (a) D. Kovala-Demertzi, *Trans. Met. Chem.*, 15 (1990) 23. (b) L.J. Bellamy, *The Infrared spectra of complex molecules*, Vol. 1, Chapman and Hall, London, 3rd edn., 1975.
- [10] A. Sánchez González, A. Castiñeiras, J.S. Casas, J. Sordo and U. Russo, *Inorg. Chim. Acta*, 216 (1994) 257.
- [11] L.E. Sutton, *Interatomic Distances*, The Chemical Society, London, 1958.