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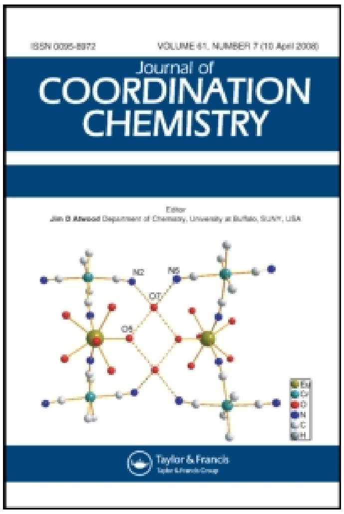

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SYNTHESIS AND CHARACTERIZATION OF A FIVE-COORDINATE 1:1 ADDUCT DERIVED FROM DIPHENYLTIN(IV) DICHLORIDE AND 6-METHOXY-2-[(4-CYANOPHENYLIMINO)METHYL|PHENOL

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SYNTHESIS AND CHARACTERIZATION OF A FIVE-COORDINATE 1 : 1 ADDUCT DERIVED FROM DIPHENYLTIN(IV) DICHLORIDE AND 6-METHOXY-2-[(4-CYANOPHENYLIMINO)METHYL]PHENOL

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Reaction of diphenyltin(IV) dichloride with 6-methoxy-2-[(4-cyanophenylimino)methyl]phenol results in the formation of an adduct with 1 : 1 (organotin : ligand) stoichiometry and coordination of the ligand to the Sn atom occurs *via* the phenolic oxygen atom. An X-ray crystal structural study of dichlorodiphenyl[6-methoxy-2-[(4-cyanophenylimino)methyl]phenol]tin(IV) has been carried out using a charge-coupled device (CCD) area detector diffractometer. The Schiff base and the resulting adduct were characterized by elemental analysis, ^{1}H, ^{13}C and ^{119}Sn NMR spectroscopies.

Keywords: 6-methoxy-2-[(4-cyanophenylimino)methyl]phenol; five-coordinate; Schiff base; charge-coupled device; X-ray structure

INTRODUCTION

Previous reports reveal that reactions of Schiff bases salicylideneimine and 2-hydroxy-1-naphthalideneimine with inorganic tin(IV) and organotin(IV) form 1 : 1 or 1 : 2 (tin : ligand) adducts depending on electronic or steric effects

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TABLE I Crystal data and details of structure refinement for $(C_6H_5)_2SnCl_2 \cdot (CH_3O)HOC_6H_3CH:NC_6H_4CN$

Formula	$C_{27}H_{22}N_2O_2Cl_2Sn$
Formula weight	596.18
Crystal system	monoclinic
Space group	$P2_1/n$
a (Å)	14.070(1)
b (Å)	13.531(1)
c (Å)	15.008(2)
β [°]	116.13(1)
V (Å^3)	2565.2(5)
Z	4
D_C	1.543
F(OOO)	1192
Number of total reflections	7093
Number of refined reflections	6768
R	0.036
R_w	0.031

in both the tin moiety or the ligand.[1-11] Interestingly, X-ray structural studies show that reactions of diorganotin(IV) with bifunctional monodentate salicylideneimine and 2-hydroxy-1-naphthalideneimine ligands yielded 1 : 2 (tin : ligand) adducts in which the Schiff bases were coordinated to the tin atom *via* the phenolic O atoms.[4,10,11,14]

However, in the course of our recent studies of the reactions of tin compounds with Schiff bases which possess various lateral substituents in the salicylaldehyde and aniline fragments, we have isolated a 1 : 1 adduct derived from diphenyltin(IV) dichloride with the bifunctional monodentate 6-methoxy-2-[(4-cyanophenylimino)methyl]phenol. A structural determination has been carried out on dichlorodiphenyl[6-methoxy-2-[(4-cyanophenylimino)methyl]phenol]tin(IV) using a charge-coupled device (CCD) diffractometer along with elemental analysis, ^1H, ^{13}C and ^{119}Sn NMR spectroscopic methods.

EXPERIMENTAL

Microanalyses were carried out on Yanaco MT-5 elemental analyzer at the Tokyo Institute of Technology. ^1H, ^{13}C and ^{119}Sn NMR spectra were recorded on a JEOL JNM-GX-500 spectrometer. 500 MHz ^1H, ^{13}C and ^{119}Sn NMR spectra were recorded at 30°C; DMSO-d_6 was used as the solvent for ^1H and ^{13}C. The ^{119}Sn NMR, on the other hand, was carried out in dichloromethane solution. Whilst tetramethylsilane (TMS) was used as internal standard for ^1H and ^{13}C NMR, tetramethyltin was used as an external chemical shift standard for ^{119}Sn NMR.

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TABLE II Atomic coordinates (× 10^4, × 10^5 for Sn and Cl) and U_{iso} (× 10^4) for non-hydrogen atoms

	x/a	y/b	z/c	U_{iso}
Sn(1)	30919(1)	28764(1)	52464(1)	417(3)
Cl(1)	34486(5)	22456(3)	39263(4)	594(3)
Cl(2)	42233(4)	15426(4)	63794(5)	713(3)
O(2)	1905(1)	4461(1)	5646(1)	555(7)
O(1)	2159(1)	3935(1)	4041(1)	463(6)
N(1)	1719(1)	4205(1)	2181(1)	426(7)
N(2)	2037(2)	2455(2)	−1886(2)	892(13)
C(26)	1947(2)	2862(1)	1257(2)	515(10)
C(21)	1759(1)	3862(1)	1309(1)	425(8)
C(20)	1226(1)	4996(1)	2257(1)	430(8)
C(14)	1453(1)	5048(1)	4831(1)	436(8)
C(24)	1890(1)	3126(2)	−345(1)	507(9)
C(23)	1698(2)	4119(2)	−286(2)	577(11)
C(22)	1636(2)	4489(1)	543(2)	545(10)
C(25)	2013(2)	2494(2)	432(2)	547(10)
C(15)	875(2)	5889(2)	4765(2)	544(10)
C(17)	551(2)	6153(1)	3080(2)	542(10)
C(27)	1971(2)	2747(2)	−1207(2)	617(12)
C(16)	419(2)	6432(2)	3882(2)	609(11)
C(13)	1606(1)	4724(1)	4010(1)	394(8)
C(18)	1146(1)	5287(1)	3119(1)	411(8)
C(1)	1670(2)	2209(1)	5132(2)	454(8)
C(7)	4193(2)	4009(1)	6040(2)	486(9)
C(6)	717(2)	2383(2)	4321(2)	563(11)
C(12)	4195(2)	4905(2)	5614(2)	671(12)
C(2)	1685(2)	1583(1)	5873(2)	591(11)
C(8)	4874(2)	3886(2)	7031(2)	813(14)
C(5)	−205(2)	1934(2)	4237(3)	733(14)
C(4)	−171(3)	1320(2)	4979(3)	781(16)
C(11)	4857(2)	5663(2)	6170(3)	823(16)
C(3)	757(3)	1152(2)	5791(3)	744(15)
C(10)	5511(2)	5527(2)	7150(3)	822(16)
C(9)	5515(3)	4655(3)	7579(3)	1016(18)
C(19)	2035(3)	4836(2)	6579(2)	717(15)

Preparation of 6-Methoxy-2-[(4-cyanophenylimino)methyl]phenol (OVACYA)

A solution of *o*-vanilin (15.22 g, 0.1 mol) in mixed solvent of 95% ethanol and dichloromethane (1 : 1) was added to 4-cyanoaniline (11.81 g, 0.1 mol) in the same solvent. The mixture was stirred and a yellow to red solid precipitated; m.p. 149–150°C. Anal.: Calcd. for $C_{15}H_{12}N_2O_2$ (%): C, 71.41, H, 4.80, N, 11.10. Found: C, 71.40, H, 4.80, N, 11.15; NMR (^{1}H, DMSO-d_6, 30°C): δ, 12.46(s, 1H, OH), 8.96(s, 1H, CH=N); (^{13}C, DMSO-d_6, 30°C): δ, 152.4(CH : N), 165.4(C–O, phenol).

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TABLE III Selected bondlengths (Å) and angles (°) with esd's in parentheses

Sn1-Cl1	2.404(1)	C24-C25	1.393(3)
Sn1-Cl2	2.510(1)	C24-C27	1.441(4)
Sn1-O1	2.226(1)	C23-C22	1.378(4)
Sn1-C1	2.132(2)	C15-C16	1.400(3)
Sn1-C7	2.131(2)	C17-C16	1.351(4)
O2-C14	1.360(2)	C17-C18	1.426(3)
O2-C19	1.423(3)	C13-C18	1.422(2)
O1-C13	1.310(2)	C1-C6	1.378(3)
N1-C21	1.414(3)	C1-C2	1.391(4)
N1-C20	1.306(3)	C7-C12	1.372(3)
N(H)-O1	1.907(2)	C7-C8	1.379(3)
N2-C27	1.135(4)	C6-C5	1.387(4)
C26-C21	1.388(3)	C12-C11	1.391(3)
C26-C25	1.375(4)	C2-C3	1.385(5)
C21-C22	1.376(3)	C8-C9	1.385(4)
C20-C18	1.405(3)	C5-C4	1.373(5)
C14-C15	1.376(3)	C4-C3	1.357(4)
C14-C13	1.411(3)	C11-C10	1.360(4)
C24-C23	1.382(3)	C10-C9	1.343(5)
Cl1-Sn1-CL2	90.2(0)	C14-C15-C16	120.8(3)
Cl1-Sn1-O1	79.7(0)	C16-C17-C18	120.1(2)
Cl1-Sn1-CL1	108.2(1)	N2-C27-C24	179.5(3)
Cl1-Sn1-C7	110.6(1)	C15-C16-C17	120.7(2)
Cl2-Sn1-O1	169.8(0)	O1-C13-C14	122.6(2)
Cl2-Sn1-C1	92.4(1)	O1-C13-C18	119.2(2)
Cl2-Sn1-C7	92.9(1)	C14-C13-C18	118.2(2)
O1-Sn1-C1	90.6(1)	C20-C18-C17	118.4(2)
O1-Sn1-C7	90.9(1)	C20-C18-C13	121.9(2)
C1-Sn1-C7	140.8(1)	C17-C18-C13	119.7(2)
C14-O2-C19	118.9(2)	Sn1-C1-C6	120.8(2)
Sn1-O1-C13	133.0(1)	Sn1-C1-C2	120.7(1)
C21-N1-C20	126.0(2)	C6-C1-C2	118.5(2)
C21-C26-C25	119.6(2)	Sn1-C7-C12	121.7(1)
N1-C21-C26	117.3(2)	Sn1-C7-C8	120.4(2)
N1-C21-C22	122.0(2)	C12-C7-C8	117.8(2)
C26-C21-C22	120.7(2)	C1-C6-C5	120.8(2)
N1-C20-C18	124.8(2)	C7-C12-C11	120.7(2)
O2-C14-C15	125.1(2)	C1-C2-C3	120.2(2)
O2-C14-C13	114.4(2)	C7-C8-C9	120.8(3)
C15-C14-C13	120.5(2)	C6-C5-C4	119.7(2)
C23-C24-C25	119.9(2)	C5-C4-C3	120.4(3)
C23-C24-C27	120.0(2)	C12-C11-C10	120.3(3)
C25-C24-C27	120.2(2)	C2-C3-C4	120.4(3)
C24-C23-C22	120.2(2)	C11-C10-C9	119.7(3)
C21-C22-C23	119.7(2)	C8-C9-C10	120.7(3)
C26-C25-C24	119.9(2)		

Preparation of Dichlorodiphenyl[6-Methoxy-2-[(4-cyanophenylimino)methyl]phenol]tin (IV) (P2OVACYA)

The synthesis was carried out by adding a solution of Ph_2SnCl_2 (3.43 g, 10 mmol) in dichloromethane to a solution of **OVACYA** (5.04 g, 20 mmol)

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in the same solvent. Stirring of the solution and slow evaporation at room temperature gave reddish crystals; m.p. 168–169°C. Anal.: Calcd. for $C_{27}H_{22}N_2O_2Cl_2Sn$ (%): C, 54.39, H, 3.73, N, 4.70. Found: C, 54.57, H, 3.73, N, 4.68; NMR (^{1}H, DMSO-d_6, 30°C): δ, 12.47(s, 1H, OH), 8.96(s, 1H, CH=N); (^{13}C, DMSO-d_6, 30°C): δ, 152.4(CH : N), 166.0(C–O, phenol); (^{119}Sn, CH_2Cl_2, 30°C): δ, −48.56(s).

Crystal Structure Determination of dichlorodiphenyl[6-Methoxy-2-[(4-cyanophenylimino)methyl]phenol]tin(IV) (P2OVACYA)

A suitable reddish crystal was obtained by recrystallization from dichloromethane and hexane. Intensity data for the crystal with dimensions 0.35 × 0.40 × 0.28 mm were measured at room temperature on a CCD

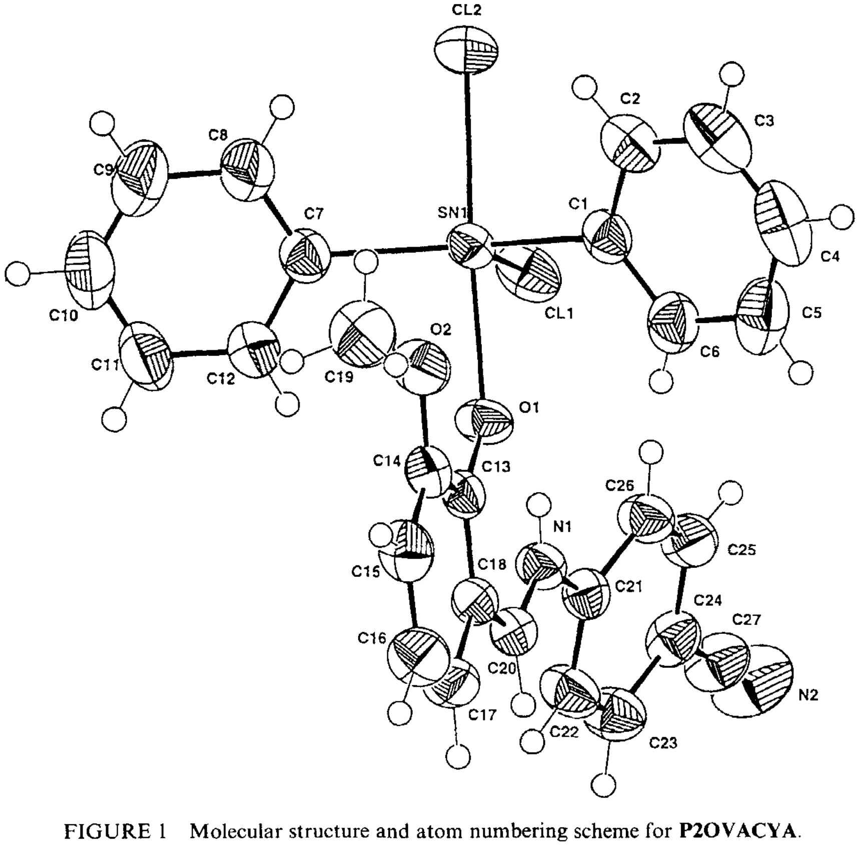

FIGURE 1 Molecular structure and atom numbering scheme for **P2OVACYA**.

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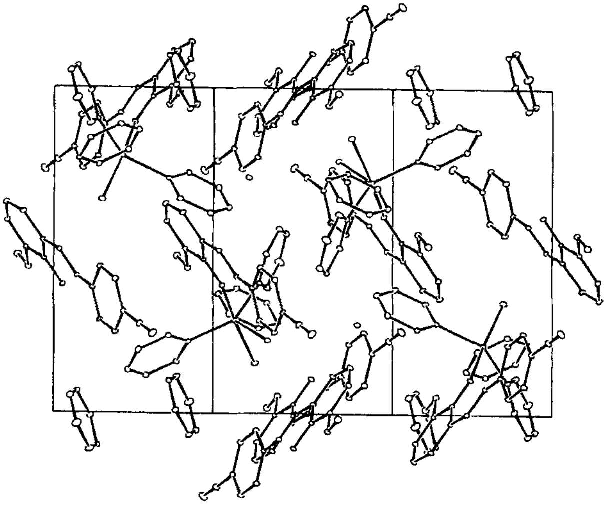

FIGURE 2 Projection of a crystal packing of molecules of **P2OVACYA** on the *ab* plane.

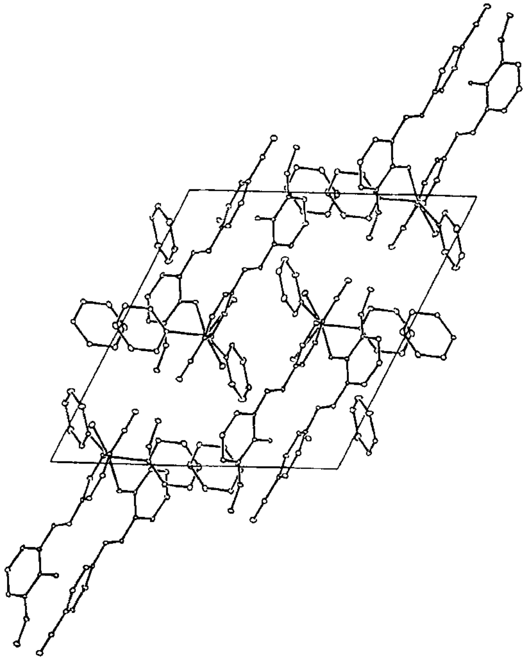

FIGURE 3 Projection of a crystal packing of molecules of **P2OVACYA** on the *ac* plane.

diffractometer (Siemens SMART system) fitted with graphite-monochromated MoKα radiation, $\lambda = 0.71073$ Å. The ω scan method was employed to measure a total of 7093 reflections such that $\theta_{max} < 31°$. The crystals of **P2OVACYA** are monoclinic with space group $P2_1/n$ with $a = 14.070(1)$, $b = 13.531(1)$, $c = 15.008(1)$ Å, $\beta = 116.13(1)°$. No significant decomposition occurred during the data collection. Lattice parameters were derived by a least-squares treatment of the measured angles for 19633 reflections.

The structure was solved by direct methods and refined by full-matrix least-squares methods based on F with anisotropic displacement parameters for the non-H atoms. The positions of the H atoms were found in different Fourier maps and refined using isotropic displacement parameters. An empirical extinction correction was applied to F_C based on the Zachariasen formula.[12] The refinement continued to final $R = 0.036$ and $R_W = 0.031$ for 6768 independent reflections. As for the weighing scheme, $1/\sigma(|F_O|)$ was used. The XTAL programs package[13] was used for structure solution and refinement. Crystal data are listed in Table I. Fractional atomic coordinates and thermal parameters of **P2OVACYA** are given in Table II. Selected bond lengths and angles are listed in Table III. Details of the crystal structure determination are available on request from the authors.

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RESULTS AND DISCUSSIONS

The adduct **P2OVACYA** derived from the reaction of diphenyltin(IV) dichloride with **OVAVYA** crystallized with a tin to ligand ratio of 1 : 1. This adduct is stable in ambient temperature with melting point 168–169°C as compared to the uncoordinated Schiff base (149–150°C).

The structure of the adduct **P2OVACYA** and the atom labelling scheme is illustrated in Figure 1. It is clearly seen that the central core of the Schiff base consists of the exocyclic –C=N– bond. However, the planes of the phenyl rings are tilted with respect to each other by 26.44° upon coordination to the Sn atom. The geometry about the Sn atom is trigonal bipyramidal with a Cl atom and the ipso-carbon atoms of the phenyl groups lying in the equatorial plane. The other Cl atom from a Ph_2SnCl_2 moiety and the O atom from the Schiff base occupy *trans* apical sites.

One of the notable features of the structure is that the phenolic H atom has migrated to the imine N atom which forms part of the stable six membered ring. The N(H)–O bond distance of 1.907 (2) Å (Table III) indicates a weak hydrogen bond as reported in adducts derived from Me_2SnCl_2

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with 1-(3-methoxyphenylimino)methyl-2-naphthol[14] and 1-(4-methylphenylimino)methyl-2-phenol.[11] This phenomenon of intramolecular hydrogen bonding was well substantiated by Bullock and coworkers.[15] The creation of this favourable condition for a proton migration is found to be important particularly towards constructing required nitrobenzilidene derivatives of *o*-amidoanilines.[16]

It has been reported that Schiff bases in adducts derived from the reactions of Me_2SnCl_2 with 1-(3-methoxyphenylimino)methyl-2-naphthol and 1-(4-methylphenylimino)methyl-2-phenol exist as zwitterions. Thus, the ligand in the present structure is also a zwitterion derived from the Schiff base which coordinates to the Sn *via* the phenolic O atom. It is also found that the Sn–Cl2 distance 2.510(1) Å is greater than that in the equatorial position (2.404(1) Å). The elongation of the axial Sn–Cl bond can be ascribed to a more effective interaction between the *p* orbital of the Cl atom and a filled d_{z^2} orbitals of Sn atom which results in stronger electronic repulsion.[17,18] The C–N distance of the cyano group, 1.135(4) Å, is close with that in 4-bromo-2,6-dichlorobenzonitrile (1.154(7) Å).[19] The Cl2–Sn1–O1 bond angle, 169.9 (0)°, shows distorted trigonal bipyramidal geometry around the Sn atom.

Microanalytical data for the uncoordinated Schiff base and the resulting adduct with Ph_2SnCl_2 are consistent with their formulations. The molecular structure of the title compound is supported by the 500 MHz ^1H, ^{13}C and ^{119}Sn NMR. Inspection of the ^1H NMR spectrum of **P2OVACYA** shows a sharp peak ascribed to the azomethine proton at 8.96 ppm, almost unaltered in comparison with the spectrum of the uncoordinated Schiff base. Broadening of the O–H peak centred at 12.47 ppm is observed, due to weakening of the O–H and strenthening of the N–H bond. This indicates the participation of the O atom in coordination to the Sn atom. Further evidence regarding the participation of phenolic oxygen in the coordination of the tin atom can be inferred from ^{13}C NMR in which the peak due to C13 (bonded to the phenolic oxygen atom) of the ligand is shifted by 0.6 ppm. A peak which appears in the ^{119}Sn NMR spectrum is located within the range of chemical shifts as reported for five-coordinate complexes.[20]

Molecular Packing

The molecular packing within the unit cell of **P2OVACYA** is illustrated in Figures 2 and 3 in which the hydrogen atoms have been removed for clarity. It is clear in Figure 2 that the molecules exist in stacks wherein each stack is composed of molecules generated by inversion centres without any intermolecular contact. In addition, the molecules within each stack as projected along the *b* axis (Figure 3) show the Schiff bases oriented in opposite directions whereas the aldehyde fragment is found lying side by side with the aniline fragment from an adjacent molecule.

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References

[1] J.N.R. Ruddick and J.R. Sams, *J. Organomet. Chem.*, **60**, 233 (1973).
[2] T.N. Srivastava and A.K.S. Chauhan, *J. Inorg. Nucl. Chem.*, **39**, 371 (1977).
[3] B.S. Saraswat, G. Srivastava and P.C. Mehrotra, *Inorg. Chim. Acta*, **36**, 289 (1979).
[4] M.E. Kamwaya and L.E. Khoo, *Acta Cryst.*, **C41**, 1027 (1985).
[5] B.K. Dwivedi, K. Bhatnagar and A.K. Srivastava, *Synth. React. Inorg. Met. Org. Chem.*, **16**, 715 (1986).
[6] H.K. Fun, S.B. Teo, S.G. Teoh and G.Y. Yeap, *Acta Cryst.*, **C47**, 1845 (1991).
[7] H.K. Fun, S.B. Teo, S.G. Teoh, G.Y. Yeap and T.S. Yeoh, *Acta Cryst.*, **C47**, 1602 (1991).
[8] S.G. Teoh, S.B. Teo and G.Y. Yeap and J.P. Declercq, *J. Coord. Chem.*, **25**, 327 (1992).
[9] S.G. Teoh, S.B. Teo, G.Y. Yeap, H.K. Fun and P.J. Smith, *J. Organomet. Chem.*, **454**, 73 (1993).
[10] S.G. Teoh, G.Y. Yeap, S.B. Teo and H.K. Fun, *Acta Cryst.*, **14**, 1051 (1995).
[11] G.Y. Yeap, S.G. Teoh, S.B. Teo, S.C. Loh and H.K. Fun, *Polyhedron*, **15**, 3941 (1996).
[12] W.H. Zachariasen, *Acta Cryst.*, **23**, 558 (1967).
[13] S.R. Hall, G.S.D. King and J.M. Stewart, Eds., "Xtal 3.4 User's Manual" (University of Western Australia, Perth).
[14] S.G. Teoh, S.B. Teo, G.Y. Yeap and J.P. Declercq, *Polyhedron*, **10**, 2683 (1991).
[15] J.I. Bullock, M.F.C. Ladd, D.C. Povey and H.A. Tajmir-Riahi, *Acta Cryst.*, **B35**, 2013 (1979).
[16] S.M. Aldoshin, I.I. Chuev and O.A. Kozina, *Mol. Cryst. Liq. Cryst.*, **264**, 215 (1995).
[17] C.A.L. Becker, D.W. Meek and T.M. Bunn, *J. Phys. Chem.*, **72**, 3588 (1968).
[18] J.S. Wood, *J. Chem. Soc.*, A, 1582 (1969).
[19] D. Britton, *Acta Cryst.*, **C53**, 225 (1997).
[20] J. Otera, T. Hinoishi and R. Okawara, *J. Organomet. Chem.*, **202**, C93 (1980).

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