Studies on the Interaction of Inorganic Tin Compounds with Methyl 4,6-*O*-benzylidene-α-D-glucopyranoside and Related Molecules

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The interaction of inorganic tin(IV) and tin(II) compounds with methyl 4,6-O-benzylidene-α-D-glucopyranoside and other polyhydroxylated molecules has been studied in the solid state and in solution.

Attempts to prepare tin(IV) and tin(II) derivatives containing Sn–O bonds were unsuccessful, except when severe conditions (high temperatures and extended reaction times) were used. An unstable solid 1:1 adduct of $SnCl_4$ *with methyl 4,6-O-benzylidene-α-D-glucopyranoside was isolated from non-coordinating solvents (*e.g. $CHCl_3$*), and, in this complex, the sugar molecule acts as a neutral bidentate oxygen donor ligand.*

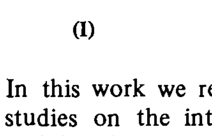
The reaction of $SnCl_4$ *or* $SnCl_2$ *with methyl 4,6-O-benzylidene-α-D-glucopyranoside in methanol results in cleavage of the benzylidene moiety from the pyranoside ring to give methyl α-D-glucopyranoside and benzaldehyde dimethyl acetal.*

A mechanism for the catalytic monomethylation of vicinal diols by the $SnCl_2/CH_2N_2/MeOH$ *system is proposed.*

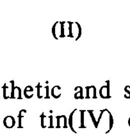
Introduction

Although there has been considerable interest in di- and tri-*O*-butylstannyl ethers of carbohydrates [1–10], there has been only one report on the inorganic tin derivatives [10a]. An investigation of the interaction of inorganic tin compounds with carbohydrates and related molecules is of considerable importance in connection with their use as homogeneous catalysts for the selective methylation and diphenylmethylation of polyhydroxylated derivatives, using $SnCl_2/CH_2N_2$ [11–19] and $SnCl_2/CPh_2N_2$ [20–23], and as potential flame-resist treatments for cellulosic polymers, such as cotton [24, 25].

The selective monomethylation of vicinal diols has been achieved by the use of diazomethane in the presence of catalytic amounts of an inorganic tin salt, usually $SnCl_2$, in methanol solution [11–19]. In particular, methylation of the monosaccharide, methyl 4,6-*O*-benzylidene-α-D-glucopyranoside (I), using the $SnCl_2/CH_2N_2$ reagent, gives a 97% yield of the 3-*O*-methyl ether [11]. It has recently been shown [19] that stannous chloride reacts with diazomethane in methanol to produce bis(methoxy)-tin(II), $Sn(OMe)_2$, which catalyses the monomethylation reaction, and it has been suggested [3, 13, 19] that this species reacts with the vicinal diol system to form a cyclic inorganic tin(II) ether (II), which may account for the selective activation of the vicinal hydroxy groups.



(I)



(II)

In this work we report synthetic and spectroscopic studies on the interaction of tin(IV) chloride and tin(II) chloride with methyl 4,6-*O*-benzylidene-α-D-glucopyranoside and with related hydroxyl compounds in coordinating and non-coordinating organic solvents.

Experimental

Syntheses

Tetrachloro(methyl 4,6-O-benzylidene-α-D-glucopyranoside)tin(IV)

A solution of anhydrous stannic chloride (1 ml; 0.009 mol) in chloroform (20 ml) was added to a stirred solution of (I) (2.4 g; 0.009 mol, in 40 ml) in the same solvent, under dry nitrogen, and the resulting off-white solid was removed by filtration, dried *in vacuo*, and stored in a sealed tube. Found: C, 31.6; H, 4.5; Sn, 19.8. Calc. for $C_{14}H_{18}O_6Cl_4Sn$: C, 31.0; H, 3.3; Sn, 21.9%.

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Glyceroxytin(II)

This compound was prepared by the high temperature reaction of blue-black stannous oxide and glycerol, under dry nitrogen [26]. The grey solid obtained was washed with water and dried *in vacuo* at room temperature. M.p. > 300 °C. Found: C, 13.9; H, 1.9. Calc. for $C_6H_{10}O_6Sn_3$: C, 13.5; H, 1.9%.

Tetrachlorobis(1,2-ethanediol)tin(IV)

This compound was prepared according to the method of Pfeiffer [27].

Diaquatetrachlorotin(IV)–1,4-dioxan (1/2)

$SnCl_4(H_2O)_2 \cdot 2diox$ was synthesised as previously reported by Barnes and Weakley [28].

Tetrachlorobis(cyclohexanol)tin(IV)–cyclohexanol (1/2)

$SnCl_4(CyOH)_2 \cdot 2CyOH$ was obtained according to the method of Fournet and Theobald [29].

Spectroscopic Methods

^{119}Sn Mössbauer spectra were recorded at 80 K, using a constant acceleration microprocessor spectrometer described previously [30]. The experimental error in the measured values of isomer shift (δ) and quadrupole splitting (ΔE_Q) parameters is ±0.02 mm s^{-1}. Isomer shifts are relative to $CaSnO_3$.

^{13}C NMR spectra were recorded at 30 °C, on Nicolet NT 200 or Varian XL 200 instruments in 10 mm tubes. ^{13}C chemical shifts ($\delta(^{13}C)$) are relative to TMS and are accurate to ±0.1 ppm.

^{119}Sn NMR spectra were measured in 10 mm tubes at 25 °C on a JEOL FX 90Q spectrometer. ^{119}Sn chemical shifts ($\delta(^{119}Sn)$) are relative to Me_4Sn and are accurate to ±0.5 ppm.

Field frequency lock, for recording ^{13}C and ^{119}Sn NMR spectra, was to the solvent CD_3OD, or to external $(CD_3)_2CO$ in a concentric 5 mm tube.

Infrared spectra were recorded as Nujol mulls on a Pye-Unicam SP 2000 instrument.

Results and Discussion

Tin(IV) Compounds

Since di- and tri-*O*-butylstannyl ethers of carbohydrates have been well characterised [1–10], attempts were made to synthesise the analogous inorganic tin(IV) derivatives. Unfortunately, several preparative routes to these compounds were unsuccessful [31], indicating that the formation of Sn–O bonded products is not favoured in these systems. However, on mixing equimolar solutions of anhydrous $SnCl_4$ and (I) in a non-coordinating solvent, such as chloroform or dichloromethane, a neutral 1:1 adduct, $SnCl_4(I)$, which rapidly decomposes in air, is formed. ^{119}Sn Mössbauer data for this complex, and for some related tin(IV) chloride adducts, are given in Table I. The Mössbauer isomer shifts for the $SnCl_4$ adducts with hydroxyl donor ligands lie in the range 0.25–0.45 mm s^{-1} (Table I), and are lower than that of tin(IV) chloride itself, indicating that the *s*-electron density at the tin nucleus decreases when $SnCl_4$ complexes with hydroxyl donor ligands, as noted previously [35].

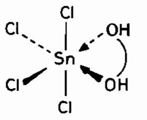
It has been suggested by Harrison *et al.* [36] that, for octahedral $SnCl_4$ adducts with *O*-donor ligands, a *trans*-configuration of the oxygen atoms results in a resolvable quadrupole splitting in the Mössbauer spectrum, whilst no ΔE_Q is observed for those complexes with a *cis*-arrangement of the oxygen donors. In agreement with this, the compounds which have been shown by X-ray crystallography to contain a *cis*-octahedral $SnCl_4L_2$ unit, *viz.* $SnCl_4(H_2O)_2 \cdot 2diox$ [28], and $SnCl_4(H_2O)_2 \cdot 3H_2O$ [34], show a single Mössbauer line, whereas $SnCl_4(CyOH)_2 \cdot 2CyOH$, in which the two coordinated cyclohexanol molecules are known to be occupying *trans*-positions [29], shows a ΔE_Q value of 0.89 mm s^{-1} (Table I). In addition, the Mössbauer spectra of the 1:2 adducts of

Table I. ^{119}Sn Mössbauer Data for Tin(IV) Chloride Adducts with Hydroxyl Ligands.

Compound	δ (mm s^{-1})	ΔE_Q(mm s^{-1})	Ref.	Configuration by X-ray Crystallography
$SnCl_4(I)$	0.32	0.00	a	–
$SnCl_4(OH \cdot CH_2 \cdot CH_2 \cdot OH)_2$	0.35	0.00	a	–
$SnCl_4(H_2O)_2 \cdot 2diox$	0.26	0.00	a	*cis*[b]
$SnCl_4(CyOH)_2 \cdot 2CyOH$	0.33	0.89	a	*trans*[c]
$SnCl_4$	0.78	0.00	32	–
$SnCl_4(H_2O)_2 \cdot 3H_2O$	0.30	0.00	33	*cis*[d]
$SnCl_4(MeOH)_2$	0.43	0.70	35	–
$SnCl_4(EtOH)_2$	0.33	0.70	35	–

[a]This work. [b]Ref. 28. [c]Ref. 29. [d]Ref. 34.

$SnCl_4$ with methanol and ethanol, show [35] a small splitting, which is presumably indicative of a similar *trans*-octahedral stereochemistry. The absence of a resolvable ΔE_Q in the Mössbauer spectrum of the sugar adduct, $SnCl_4$(I) (Table I), suggests that the carbohydrate molecule is functioning as a bidentate OH- donor ligand towards the tin atom, with the oxygen atoms occupying *cis*-positions in an octahedral monomeric structure (III):



(III)

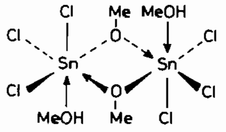
It is interesting to note that the reaction product of tin(IV) chloride and 1,2-ethanediol, shown by Pfeiffer [27] to be the 1:2 adduct, $SnCl_4(OH{\cdot}CH_2{\cdot}CH_2{\cdot}OH)_2$, gives a single Mössbauer resonance (Table I), indicating that the alcohol molecules (which presumably act as monodentate ligands) are occupying *cis*-positions about octahedral tin(IV).

In contrast to the reaction in non-coordinating solvents, the addition of $SnCl_4$ to a solution of (I) in methanol does not lead to the formation of a neutral adduct, but results in cleavage of the benzylidene moiety from the glucose ring. This is shown by the ^{13}C NMR spectrum of a 1:1 mixture of $SnCl_4$ and (I) in CD_3OD, where the chemical shifts of the pyranoside ring carbon atoms indicate the presence of methyl α-D-glucopyranoside (Table II). On cooling the solution to 0 °C, crystals of pure methyl α-D-glucopyranoside were indeed isolated in good yield, m.p. 166–8 °C (lit. [39] 166–8 °C). Found: C, 43.3; H, 6.8 Calc. for $C_7H_{14}O_6$: C, 43.3; H, 7.3%.

Cleavage of the benzylidene group from sugars in the presence of $SnCl_4$ has not been observed previously and may be caused by HCl in the solution, which is liberated when the $SnCl_4$ reacts with methanol to form a methoxytin(IV) species [40]:

$$SnCl_4 + MeOH \longrightarrow Cl_3Sn(OMe) + HCl$$

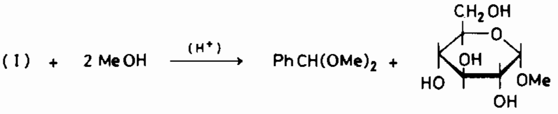
A ^{119}Sn NMR spectrum of a 30% v/v solution of $SnCl_4$ in CD_3OD shows a single resonance at –600.5 ppm, which is markedly upfield from that of tetrahedral $SnCl_4$ {for which $\delta(^{119}Sn) = -150$ ppm, as neat liquid [41]}, indicating that the species present is likely to contain a 6-coordinate tin atom {*cf.* $SnCl_4(PBu_3)_2$, $\delta(^{119}Sn) = -573$ ppm, in CH_2Cl_2 [42]}. In line with this observation, $Cl_3Sn(OMe)$ has previously been isolated in the solid state as an alcohol solvate, $Cl_3Sn(OMe){\cdot}MeOH$, and this has been shown [43] by X-ray crystallography to exist as a methoxy-bridged dimer (IV), containing octahedrally coordinated tin atoms:



(IV)

The ^{13}C NMR spectrum of a solution of $SnCl_4$ in methanol does not show a resonance corresponding to a methoxy group attached to the tin atom, although this may be due to rapid exchange of the OMe moieties in solution. This is in accord with the work of Davies *et al.* [44], who observed a similar exchange of alkoxy groups in solution, for a series of tributyltin alkoxides, except for those in which the alkoxy moieties were very bulky.

Acid cleavage of the benzylidene group from (I) might be expected to give benzaldehyde, PhCHO. However, it is known [45] that, under acidic conditions, aldehydes react with alcohols to form acetals and therefore, in this case, the reaction product is expected to be benzaldehyde dimethyl acetal, $PhCH(OMe)_2$:



A ^{13}C NMR spectrum of the $SnCl_4$/(I) solution in methanol shows, as well as the peaks associated with methyl α-D-glucopyranoside (Table II), six additional resonances, and it is found that these correspond to an authentic equimolar $SnCl_4/PhCH(OMe)_2$ solution (Table III).

It is known [46] that 1,2-dimethoxyethane, $MeOCH_2CH_2OMe$, forms a neutral 1:1 adduct with $SnCl_4$ and, consequently, it would be expected that

TABLE II. ^{13}C NMR Chemical Shifts[a] for the Pyranoside Ring and C-1 Methoxy Carbon Atoms of the Reaction Products of $SnCl_4$ and $SnCl_2$ with (I) in CD_3OD.

Solution	C_1	C_2	C_3	C_4	C_5	C_6	OMe
(I)[b]	101.9	73.9	71.9	82.7	63.8	69.9	55.7
$SnCl_4$/(I)	101.1	73.5	75.1	71.8	73.3	62.7	55.6
$SnCl_2$/(I)[c]	101.1	73.4	75.1	71.7	73.4	62.6	55.5
Methyl α-D-glucopyranoside[d]	101.2	73.5	75.1	71.7	73.5	62.6	55.5

[a] In ppm (± 0.1) downfield from Me_4Si. [b] Chemical shift assignments according to ref. 37. [c] Spectrum recorded $1\frac{1}{2}$ hr after mixing. [d] Chemical shift assignments according to ref. 38.

TABLE III. ^{13}C NMR Chemical Shifts[a] for the $SnCl_4/PhCH(OMe)_2$ Systems in MeOH.

Solution	Ph	$\geqslant$CH	OMe
$SnCl_4$/(I)	139.2, 129.4, 129.0, 127.6	104.7	53.3
$SnCl_4/PhCH(OMe)_2$	139.1, 129.4, 129.0, 127.5	104.6	53.4
$PhCH(OMe)_2$	139.3, 129.4, 129.0, 127.7	104.4	53.0

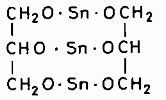
[a] In ppm (±0.1) downfield from Me_4Si.

the $PhCH(OMe)_2$ formed in the $SnCl_4$/(I) reaction would complex with the tin(IV) species present, in a similar manner. Comparison of the ^{13}C NMR resonances of the $SnCl_4/PhCH(OMe)_2$ solution with those of a solution of $PhCH(OMe)_2$, (Table III), reveals that a small downfield shift of the -OMe and $\geqslant$CH carbon atoms occurs in the former case, and this may be due to deshielding of these carbon nuclei through complexation involving electron donation from oxygen to tin. Additionally, a ^{119}Sn NMR spectrum of the $SnCl_4$/(I) solution in CD_3OD shows a peak at –603.6 ppm, characteristic of a 6-coordinate tin(IV) moiety [42].

Tin(II) Compounds

It has been suggested [3, 13, 19] that the selective methylation of vicinal diols, using the $SnCl_2/CH_2N_2$ reagent in methanol, involves a cyclic inorganic tin(II) intermediate (II) and, consequently, attempts have been made to isolate and characterise a tin(II) derivative of (I). Unfortunately, as in the case of tin(IV), several preparative routes to this compound were unsuccessful [31], indicating that the formation of Sn–O bonded products is not favoured under mild reaction conditions.

However, the high temperature reaction of blue-black SnO and glycerol, $CH_2OH{\cdot}CHOH{\cdot}CH_2OH$, under dry nitrogen, previously reported by Blewett and Rhodes [26], has been confirmed, and microanalytical data for the solid grey product are consistent with the idealised structure (V):



$$\begin{array}{ccc} CH_2O\cdot Sn\cdot OCH_2 \\ | \qquad\qquad | \\ CHO\cdot Sn\cdot OCH \\ | \qquad\qquad | \\ CH_2O\cdot Sn\cdot OCH_2 \end{array}$$

(V)

The infrared spectrum of this compound shows strong bands at 1070 cm^{-1} and 605 cm^{-1}, attributed to ν(Sn–O–C) and ν(Sn–O) respectively, {*cf.* $Sn(OMe)_2$, which shows [47] ν(Sn–O–C) at 1025 cm^{-1} and ν(Sn–O) at 570 cm^{-1}}. The ^{119}Sn Mössbauer parameters for glyceroxytin(II), *viz.* $\delta = 2.90$ mm s^{-1}; $\Delta E_Q = 1.85$ mm s^{-1}, are similar to those observed for (1,2-phenylenedioxy)tin(II) ($\delta = 2.95$ mm s^{-1}; $\Delta E_Q = 1.76$ mm s^{-1}) [48], the low value of δ being consistent with extensive use of *s*-electron density in the bonding of the tin to the oxygen atoms of the organic molecule, and the large ΔE_Q, of a highly asymmetric tin(II) environment. Additionally, severe reaction conditions have recently been found necessary to prepare the tin(II) derivative of 1,2-ethanediol [49].

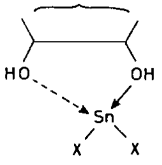
As in the case of $SnCl_4$, it was not possible to isolate a neutral adduct from an equimolar solution of $SnCl_2$ and (I), or $SnCl_2$ and methyl α-D-glucopyranoside, in methanol, although Pellerito *et al.* [50] have recently synthesised a series of neutral 1:1 adducts of $SnCl_2$ with the nucleosides, adenosine, inosine and cytidine, in this solvent. A ^{13}C NMR spectrum of an equimolar $SnCl_2$/(I) solution in CD_3OD, recorded shortly after mixing, indicates that no apparent reaction has occurred. However, a spectrum recorded on the same solution 0.5 hr after mixing shows the presence of both (I) and methyl α-D-glucopyranoside in approximately equal amounts and, after a further 1 hr, the ^{13}C spectrum indicates that all of the starting sugar has been converted to methyl α-D-glucopyranoside (Table II).

Since it has been shown that cleavage of the benzylidene group from (I) in the $SnCl_4$/(I)/MeOH system probably results from the formation of HCl in the solution, the slower reaction observed with tin(II) chloride may be due to the higher initial pH of the $SnCl_2$/(I) solution. The pH of a 0.7 *M* solution of $SnCl_2$ in methanol at room temperature, decreases from *ca.* 1.5 to 0.75, on standing for 1.5 hr, and is accompanied by almost complete oxidation of the tin(II) species. However, a similar $SnCl_2$ solution containing an equimolar amount of (I) is still substantially (*ca.* 50%) Sn(II) in nature, which implies that the presence of (I) appears to retard the oxidation of the stannous ions, and this may be due to the formation of a weak donor complex in solution.

Conclusions

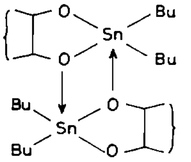
In view of these results, the following mechanism for the catalysis of the monomethylation of vicinal diols by $SnCl_2$ in diazomethane/methanol, at room temperature, may be proposed.

The intermediate tin(II) species in solution is a neutral donor adduct (VI, X = Cl or OMe) with the organic hydroxyl ligand, rather than the cyclic tin(II) ether (II) proposed earlier [3, 13, 19]:



(VI)

Since tin(II) compounds have a marked tendency to occupy a 3-coordinate pyramidal geometry [51, 52], it is probable that only one of the hydroxyl groups is directly coordinated to the metal, and that the second OH–––Sn interaction is very weak. Consequently, the coordinated OH group is selectively deactivated to electrophilic attack by Me^+. This structure is in contrast to that involved in the activation of vicinal diol groups by dibutylstannylation [5], where the intermediate species is a dimeric, oxygen-bridged, cyclic ether (VII):



(VII)

The electrophilic attack occurs at the oxygen atom not involved in intermolecular coordination to tin, *e.g.* *O*-2 in (I) [5]. Cleavage of the benzylidene moiety from (I) does not occur in the catalytic reaction involving $SnCl_2$ [11]. Similarly, the interaction of tin(IV) chloride with vicinal diols involves the formation of a neutral adduct in which the hydroxyl groups are functioning as donor ligands to the tin atom, but, in this case, the HO → Sn interactions are likely to be symmetrically disposed in the octahedral tin(IV) environment.

Further NMR studies of the interaction of inorganic tin salts with carbohydrates, in solution, are in progress and will be reported at a later date.

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References

1 I. D. Jenkins, J. P. H. Verheyden and J. G. Moffatt, *J. Am. Chem. Soc., 93,* 4323 (1971).
2 D. Wagner, J. P. H. Verheyden and J. G. Moffatt, *J. Org. Chem., 39,* 24 (1974).
3 P. J. Smith, *Chem. Ind. (London),* 1025 (1976).
4 T. Ogawa, *Kagaku To Seibutsu, 14,* 654 (1976).
5 S. David, C. Pascard and M. Cesario, *Nouveau J. Chim., 3,* 63 (1979).
6 S. David, A. Thiéffry and A. Forchioni, *Tetrahedron Lett., 22,* 2647 (1981).
7 A. J. Crowe and P. J. Smith, *J. Organomet. Chem., 110,* C 57 (1976).
8 L. Pellerito, G. Ruisi, R. Barbieri and M. T. LoGiudice, *Inorg. Chim. Acta, 21,* L 33 (1977).
9 S. J. Blunden, P. J. Smith, P. J. Beynon and D. G. Gillies, *Carbohydr. Res., 88,* 9 (1981).
10 T. Ogawa, Y. Takahashi and M. Matsui, *Carbohydr. Res., 102,* 207 (1982).
(a) J. Alföldi, R. Toman and C. Peciar, *Carbohydr. Res., 105,* 258 (1982).
11 M. Aritomi and T. Kawasaki, *Chem. Pharm. Bull. (Tokyo), 18,* 677 (1970).
12 M. J. Robins and S. R. Naik, *Biochim. Biophys. Acta, 246,* 341 (1971).
13 M. J. Robins, S. R. Naik and A. S. K. Lee, *J. Org. Chem., 39,* 1891 (1974).
14 M. J. Robins, A. S. K. Lee and F. A. Norris, *Carbohydr. Res., 41,* 304 (1975).
15 G. J. F. Chittenden, *Carbohydr. Res., 43,* 366 (1975).
16 G. J. F. Chittenden, *Carbohydr. Res., 52,* 23 (1976).
17 G. J. F. Chittenden, *Carbohydr. Res., 74,* 333 (1979).
18 G. J. F. Chittenden, *Carbohydr. Res., 91,* 85 (1981).
19 L. Dudycz, A. Kotlicki and D. Shugar, *Carbohydr. Res., 91,* 31 (1981).
20 S. Petursson and J. M. Webber, *Carbohydr. Res., 103,* 41 (1982).
21 L. F. Christensen and A. D. Broom, *J. Org. Chem., 37,* 3398 (1972).
22 D. G. Bartholomew and A. D. Broom, *J. Chem. Soc., Chem. Commun.,* 38 (1975).
23 Y. Mizuno, T. Endo and K. Ikeda, *J. Org. Chem., 40,* 1385 (1975).
24 P. A. Cusack, L. A. Hobbs, P. J. Smith and J. S. Brooks, *J. Text. Inst.,* submitted.
25 P. A. Cusack and P. J. Smith, *Rev. Si, Ge, Sn, Pb Cmpds.,* in press (1983).
26 C. W. Blewett and P. H. Rhodes, *U. S. Patent* 3, 859, 236 (1975).
27 P. Pfeiffer, *Z. Anorg. Allg. Chem., 87,* 235 (1914).
28 J. C. Barnes and T. J. R. Weakley, *J. Chem. Soc. Dalton Trans.,* 1786 (1976).
29 F. Fournet and F. Theobald, *Inorg. Chim. Acta, 52,* 15 (1981).
30 P. A. Cusack, P. J. Smith and J. D. Donaldson, *J. Chem. Soc. Dalton Trans.,* 439 (1982).
31 P. A. Cusack, *Ph.D. Thesis,* University of London (1982).
32 D. E. Williams and C. W. Kocher, *J. Chem. Phys., 52,* 1480 (1970).
33 M. Cordey-Hayes, *J. Inorg. Nucl. Chem., 26,* 915 (1964).
34 J. C. Barnes, H. A. Sampson and T. J. R. Weakley, *J. Chem. Soc. Dalton Trans.,* 949 (1980).
35 S. Ichiba, M. Mishima, H. Sakai and H. Negita, *Bull. Chem. Soc. Jpn., 41,* 49 (1968).
36 P. G. Harrison, B. C. Lane and J. J. Zuckerman, *Inorg. Chem., 11,* 1537 (1972).
37 E. Conway, R. D. Guthrie, S. D. Gero, G. Lukacs, A. M. Sepulchre, E. W. Hagaman and E. Wenkert, *Tetrahedron Lett.,* 4879 (1972).

38 D. E. Dorman and J. D. Roberts, *J. Am. Chem. Soc.*, *93*, 4463 (1971).

39 R. C. Weast (ed.), 'Handbook of Chemistry and Physics', 56th Edn., CRC Press, Cleveland, Ohio (1976).

40 D. C. Bradley, E. V. Caldwell and W. Wardlaw, *J. Chem. Soc.*. 3039 (1957).

41 J. J. Burke and P. C. Lauterbur, *J. Am. Chem. Soc.*, *83*, 326 (1961).

42 R. Colton, D. Dakternieks and C. A. Harvey, *Inorg. Chim. Acta*, *61*, 1 (1982).

43 G. Sterr and R. Mattes, *Z. Anorg. Allg. Chem.*, *322*, 319 (1963).

44 A. G. Davies, D. C. Kleinschmidt, P. R. Palan and S. C. Vasishtha, *J. Chem. Soc. (C)*, 3972 (1971).

45 J. D. Roberts and M.C. Caserio, 'Basic Principles of Organic Chemistry', Benjamin, New York (1965), p. 618.

46 J. Philip, M. A. Mullins and C. Curran, *Inorg. Chem.*, *7*, 1895 (1968).

47 J. S. Morrison and H. M. Haendler, *J. Inorg. Nucl. Chem.*, *29*, 393 (1967).

48 W. D. Honnick and J. J. Zuckerman, *Inorg. Chem.*, *17*, 501 (1978).

49 R. Nesper and H. G. von Schnering, *Z. Naturforsch., Teil B*, *37*, 1144 (1982).

50 L. Pellerito, G. Ruisi, M. T. LoGiudice, J. D. Donaldson and S. M. Grimes, *Inorg. Chim. Acta*, *58*, 21 (1982).

51 J. D. Donaldson, *Progr. Inorg. Chem.*, *8*, 287 (1967).

52 J. D. Donaldson and S. M. Grimes, *Rev. Si, Ge, Sn, Pb Cmpds.*, in press (1983).