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Studies of Silyl and Germyl Group VI Species.
Part VIII.* Synthesis and Characterization of Trimethyl-, Silyl-, Germyl- and Stannyl-methyl Derivatives of Methane- and Benzene-selenols

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Abstract

Asymmetrically substituted selenides of the type $(CH_3)_3MCH_2SeR$, where M = Si, Ge, Sn and R = CH_3 and C_6H_5, have been prepared by the reaction of Group IV halides with lithium organoselenolates and characterized by their infra-red, Raman, ^1H, ^{13}C and ^{77}Se (M = Si, Ge) NMR spectra.

Introduction

Sulfur compounds of silicon, germanium and tin have been studied extensively [1–3]. These compounds have been used as reagents in organic synthesis [4–5] and as ligands for transition metal complexes [6]. Analogous selenium compounds have received much less attention but nevertheless have already been used in organic synthesis. For example, the lithium salt of $(CH_3)_3SiCH_2SeC_6H_5$ has been used to convert halides into their homologous aldehydes [7]. Several selenium compounds have been used as ligands in the preparation of transition metal complexes [8–10]. Methyl- and phenyl-seleno and -telluro derivatives of Group IV compounds have been prepared by selenium or tellurium insertion reactions with methyl- and phenyl-lithium followed by the reaction with the corresponding halide [11–14]. However the scarcity of such work is demonstrated by the fact that some authors [15] have mistakenly made the assumption that the synthesis of lithium methylselenide, a common intermediate, was original in 1983. In this report we describe the synthesis and characterization of some neopentyl compounds of selenium.

Experimental

Apparatus

All preparations were performed using a conventional high-vacuum Pyrex-glass system equipped with greaseless stopcocks. The ^1H NMR spectra were recorded on a Bruker WP80 spectrometer operating at 80 MHz using TMS as an internal lock. The ^1H chemical shifts are displayed in Table I. The ^{13}C NMR spectra were recorded on a Bruker CPX100 multinuclear pulsed Fourier transform spectrometer operating at 22.63 MHz under ^1H noise decoupling conditions using $CDCl_3$ as an internal deuterium lock and as a standard placed at 77.0 ppm from TMS. The instrument's data processing system corrected all chemical shifts to the TMS scale. The ^{13}C chemical shifts are displayed in Table II. The ^{77}Se NMR spectra were recorded on a General Electric GN300 spectrometer operating at 57.237 MHz under ^1H noise decoupling conditions using $CDCl_3$ as an internal deuterium lock and Me_2Se as an external standard. The ^{77}Se chemical shifts are −4.01, 6.59, 199.61 and 206.78 ppm for Me_3SiCH_2SeMe, Me_3GeCH_2SeMe, Me_3SiCH_2SePh and Me_3GeCH_2SePh respectively to high frequency of Me_2Se. All NMR data were recorded on pure samples sealed in semi-micro tubes surrounded by CCl_4/TMS for ^1H NMR and $CDCl_3$ for ^{13}C and ^{77}Se NMR spectra. Infrared spectra (4000–200 cm^{-1}) were recorded on pure samples placed between CsI plates using a Perkin-Elmer 180 spectrometer. Raman spectra (3100–100 cm^{-1}) were recorded on pure samples sealed in semi-micro tubes on a Spectra-Physics Model 700 spectrometer in conjunction with a Model 164 Argon-ion laser and Model 265 Exciter Unit. Typical power output varied between 100 and 300 mW, using the 488.0 nm line. Elemental analyses were performed at Guelph Chemical Laboratories Ltd., Guelph, Ontario.

Starting Materials

Selenium (British Drug House), methyllithium (Alfa), phenyllithium (Alfa) and chloromethyl(trimethyl)silane (Laramie) were commercially available and used without further purification. Chloromethyl(trimethyl)germane was prepared by the chlorination of tetramethylgermane [16] and its purity was checked by its infrared spectrum [17]. Iodomethyl-

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TABLE I. The ^1H NMR Chemical Shifts of Me_4M, Me_3MCH_2X and Me_3MCH_2SeR (M = Si, Ge, Sn; X = Cl, I; R = Me, Ph)

Compound[a]	δMe_3M	δCH_2	$\delta SeMe$	$\delta SePh$[b]
Me_4Si	0.0			
Me_3SiCH_2Cl	0.4	2.98		
Me_3SiCH_2SeMe	0.41	2.00	2.03	
Me_3SiCH_2SePh	0.26	2.15		7.26,7.55
Me_4Ge	0.33			
Me_3GeCH_2Cl	0.66(0.33)	3.30(2.97)		
Me_3GeCH_2SeMe	0.66(0.33)	2.30(1.97)	2.40(2.07)	
Me_3GeCH_2SePh	0.50(0.17)	2.41(2.08)		7.39,7.69(7.06,7.36)
Me_4Sn	0.52			
Me_3SnCH_2I	1.59(1.07)	4.84(4.32)		
Me_3SnCH_2SeMe	1.85(1.33)	4.82(4.30)	3.0(2.48)	
Me_3SnCH_2SePh	1.04(0.52)	4.22(3.70)		7.74,8.12(7.22,7.60)

[a] All shifts are in ppm to low field of external TMS, values in parentheses indicate shifts relative to Me_4M. [b] Aromatic resonances are resolved into two envelopes for ortho and para (high field) and meta (low field) protons.

TABLE II. The ^{13}C Chemical Shifts of Me_3MCH_2X and Me_3MCH_2SePh (X = Cl, I; M = Si, Ge, Sn)

Compound[a]	δMe_3M	δCH_2	δC_x	δC_m	δC_o	δC_p	σ_R°
Me_3SiCH_2Cl	−3.56	30.41					
Me_3GeCH_2Cl	−3.43	30.74					
Me_3SnCH_2I	1.82	25.02					
Me_3SiCH_2SePh	−1.16	11.70	133.31	128.76	130.39	125.71	−0.138
Me_3GeCH_2SePh	−1.55	10.92	133.63	128.76	130.38	125.77	−0.135
Me_3SnCH_2SePh	−1.69	5.76	136.94	127.79	127.79	126.88	−0.041

[a] Shifts are to low field of external TMS.

(trimethyl)stannane was prepared by the reaction of methylene iodide (Alfa) with a zinc copper couple followed by addition of chloro(trimethyl)stannane [18]. The resulting mixture was distilled on the vacuum line into traps held at 0, −63 and −196 °C. The portion collected at −63 °C was kept and the rest discarded. The purity of $(CH_3)_3SnCH_2I$ was checked by its ^1H NMR spectrum and refractive index [18].

Synthesis

Elemental selenium (0.5 g, 6.3 mmol) was placed in a 200 ml round-bottomed flask equipped with a septum. The flask was evacuated, flushed with nitrogen and then held at −196 °C. Tetrahydrofuran (*ca.* 10 ml) was then distilled into the flask and LiR ($R = CH_3$, C_6H_5; *ca.* 8 mmol) introduced by syringe. The mixture was allowed to warm slowly to room temperature with stirring. In 20 min the mixture turned milky and then colorless (with $LiCH_3$) or to a mustard color (with LiC_6H_5). After *ca.* 1.5 h of reaction time, the solvents were distilled off and, for effective removal of tetrahydrofuran, the reaction vessel was left open to the pump for 24 h (the difficulty in removing the solvent has been attributed to a possible coordination between tetrahydrofuran and LiSeR in the solid state). With the flask held at −196 °C, diethyl ether (*ca.* 10 ml) was distilled in, followed by the $(CH_3)_3MCH_2X$ (M = Si, Ge, Sn) species in slight excess (*ca.* 8.5 mmol), from a graduated storage vessel. The reaction mixture was stirred for 3 h at room temperature after which the contents were passed through traps held at −45 °C and −196 °C. The contents of the −196 °C trap (mainly ether) were discarded. The fraction held in the trap at −45 °C (containing some tetrahydrofuran) was passed through −23 and −196 °C traps. The −23 °C portion was retained and the process repeated to get the pure product. The $(CH_3)_3MCH_2SeR$ species are heavy liquids and could only be transferred with heating from a hot-air gun. The difficulty of transferrance increased with increasing molecular weight. Typical amounts prepared were 5.7 mmol and 5.3 mmol for $(CH_3)_3SiCH_2SeR$ ($R = CH_3$ and C_6H_5 respectively), 5.0 mmol and 5.2 mmol for $(CH_3)_3GeCH_2SeR$, and 5.1 mmol and 4.8 mmol for $(CH_3)_3SnCH_2SeR$. All compounds had a pungent and persistent smell. Elemental analysis was carried out on the following as representative samples: $(CH_3)_3SiCH_2SeC_6H_5$. Found: C, 51.81; H, 6.86. Calc.: C, 49.37; H, 6.63%. $(CH_3)_3GeCH_2SeC_6H_5$. Found: C, 42.77; H, 5.91. Calc.: C, 41.74; H 5.60%.

Results and Discussion

The neopentyl compounds Me_3MCH_2SeMe and Me_3MCH_2SePh were prepared by the following sequences of reactions:

$$LiR + Se \xrightarrow[\text{tetrahydrofuran}]{1.5\ h} LiSeR \qquad (1)$$

$R = CH_3, C_6H_5$

$$LiSeR + Me_3MCH_2X \xrightarrow[\text{diethylether}]{3\ h} Me_3MCH_2SeR + LiX \qquad (2)$$

(M = Se, Ge; X = Cl and M = Sn; X = I)

The Me_3MCH_2SeR compounds are heavy liquids with persistent and pungent odors. Despite the difficulty of separating them from the solvents, particularly tetrahydrofuran, they were eventually obtained in 70–90% yields based on selenium.

NMR Spectra

The NMR spectra of the neat liquids confirm, by the lack of additional peaks and the expected integration ratios, that there are no other species containing hydrogen, carbon or selenium present in any significant amount and that we are indeed dealing with pure Me_3MCH_2SeR species in all cases. Representative spectra are displayed in Fig. 1 (the ^1H NMR spectrum of Me_3GeCH_2SePh) and Fig. 2 (the ^{13}C NMR spectrum of Me_3SiCH_2SePh). The values of the chemical shifts are given in Tables I and II along with those of related species for comparison.

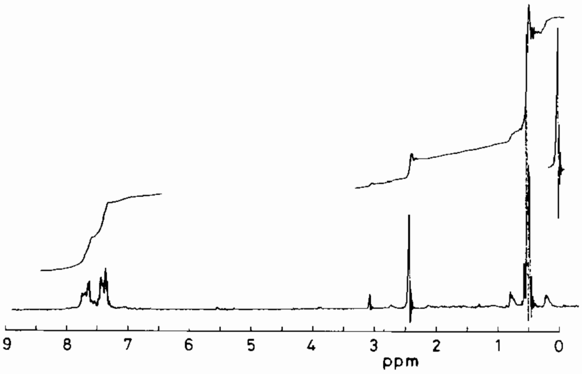

Fig. 1. The ^1H NMR spectrum of Me_3GeCH_2SePh.

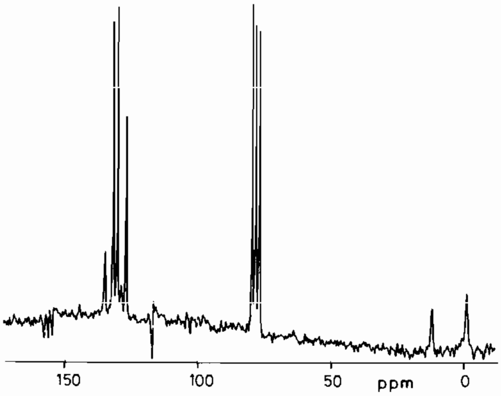

Fig. 2. The ^{13}C NMR spectrum of Me_3SiCH_2SePh.

The relationship between the ^1H NMR chemical shifts of Me_4Si, Me_4Ge, and Me_4Sn and the relative electronegativities of the Group IV elements has been the subject of considerable controversy [19–21]. The net result of the argument is the tacit agreement that the order of electronegativities is probably $Ge \geqslant Si \geqslant Sn$ despite the fact that the chemical shifts move in an almost step-wise fashion downfield of TMS. Thus, because the factors effecting the shifts are complex, it is preferrable to examine the 'internal shifts' (given in parentheses in Table I), which reflect the changes in the ^1H NMR chemical shifts relative to the parent compound, as a proton on a CH_3 group is replaced by Cl, I, SeMe or SePh, rather than the absolute values. These internal shifts might more accurately reflect changes in electronegativity. The substitution of the more electronegative chlorine atom in both Me_4Si and Me_4Ge deshields the remaining CH_2 protons to a similar extent. The effect is much less, as expected, on the other CH_3 protons, but the internal shift is greater in Me_3SiH_2Cl which contains the presumably less electronegative silicon atom. Similarly the shifts involving all substituents are largest on Me_3SnCH_2X which contains the least electronegative tin atom. In general, the shifts resulting from –SeMe or –SePh substitution suggest effective electronegativities closer to that of iodine than chlorine. The similarity in electronegativity of silicon and germanium is also indicated by the similarity in the ^{13}C NMR chemical shifts displayed in Table II for related CH_3 and CH_2 carbon atoms. For the Me_3MCH_2SePh series, the Hammett–Taft constants σ°_R [22] were calculated from $\delta_p - \delta_m = 22.06\ \sigma^\circ_R$ and found to be negative, indicating an electron release from selenium towards the phenyl ring. The ^{77}Se NMR chemical shifts are listed in the experimental section and show that the selenium atom is more shielded when attached to Me_3SiCH_2 than Me_3GeCH_2 for both–SeMe and –SePh derivatives by 9.60 and 7.17 ppm respectively. This suggests that slightly more electron density can be pulled away from a silicon-containing moiety than one containing germanium.

TABLE III. The Vibrational Spectra and the Tentative Assignments of the Series Me_3MCH_2SeMe. (M = Si, Ge, Sn)

Si		Ge		Sn		Tentative assignments
IR (liq.)	Raman (liq.)	IR (liq.)	Raman (liq.)	IR (liq.)	Raman (liq.)	
2960s	2956mw,dp	2992m	2996ms,dp	2993m	2978mw	(a) $CH_3(M)$, $CH_3(Se)$, CH_2 str.
2900sh	2893s,p	2926mw	2930s,p	2920ms	2924s	(s) $CH_3(M)$, $CH_3(Se)$, CH_2 str.
1410s	1410w,dp	1417w	1419w,dp	1428vw	1436w,dp	(a) $CH_3(M)CH_3(Se)$, CH_2 def.
1269mw	1262w	1267w	1272w	1274w	1283w	(s) CH_2 def.
1250s	1256w,p	1238w	1234w	1190w	1197w	(s) $CH_3(M)$, $CH_3(Se)$ def.
1090vs	1085vw	1085s	1082vw	1090w	1098vw	CH_2 rock
908mw	915mw	900w	909w	900m	890w	$CH_2(Se)$ rock
850mw	843vw	810s	810mn	775s	776w	$CH_3(M)$ rock
707ms	715mw,dp	600s	593m,dp	568m	563w,dp	(a) M–C str.
615s	617mw,p	570m	572p	505m	510s,p	(s) M–C str.
587m	590ms,dp	560sh	560m,dp	585ms	595m,dp	(a) Se–C str.
560w	563s,p	550w	553ms,p	575m	575m,p	(s) Se–C str.
270ms	270mw	200s	192sh	230m	233w,dp	(a) MC_3 def.
225mw	228m,p		180w,p		177w,p	(s) MC_3 def.
	180sh				153w	MC_3 rock

Vibrational Spectra

(i) Me_3MCH_2SeMe (M = Si, Ge, Sn)

The Raman spectra of this series are displayed in Fig. 3 and the frequencies and their tentative assignments are listed in Table III. The assignments were made with some confidence based on comparisons with spectra of Me_2Se [24], Me_3MSeMe [11], Me_3MCH_2X [17] and Me_nMX_{4-n} [25–27] (M = Si, Ge, Sn; n = 0–3).

As expected, the positions of the characteristic C–H vibrations were relatively unshifted upon changing M. In this region, two envelopes appear in the Raman spectra and can be assigned to the symmetric (polarized) and asymmetric (depolarized) CH_3 and CH_2 stretches in the 2920 and 2990 cm^{-1} regions respectively. When M = Ge, these two envelopes show some splitting but no attempt was made to separately assign these modes since the spectra were used for characterization rather than as a basis for a spectroscopic study. Similarly, the CH_3 and CH_2 deformation modes were assigned in the 1190–1250 cm^{-1} and 1400 cm^{-1} regions for the symmetric and asymmetric vibrations respectively. The rocking modes appear as weak bands in the Raman spectra in the 770–1100 cm^{-1} region. The C–Se and M–C stretching vibrations are easily assigned and virtually unchanged compared to those reported for the Me_3MSeMe series (M = Si, Ge, Sn) [11]. The same is noted for the MC_3 deformation and rocking modes.

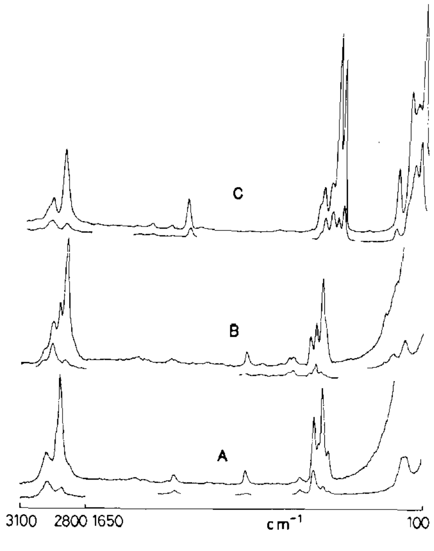

Fig. 3. The Raman spectra of Me_3SiCH_2SeMe (A), Me_3GeCH_2SeMe (B) and Me_3SnCH_2SeMe (C).

(ii) M_3MCH_2SePh (M = Si, Ge, Sn)

The Raman spectra of this series are displayed in Fig. 4. The frequencies and their tentative assignments are listed in Table IV. The vibrations associated with the Me_3MCH_2 moieties were assigned similarly to those above for Me_3MCH_2SeMe. The assignements were made assuming free rotation about the Se–Ph bond. The effective symmetry of the ring is C_{2v} which has 30 vibrations which may be labelled according to Herzberg's notation [28]. There are six substituent sensitive modes (X-Sen in Table II) which were assigned by comparison with monosubstituted benzenes [29, 30] and related molecules [13, 14, 31, 32] such as Me_3MSePh and Me_3MTePh. The remaining 24 substituent-insensitive vibrations may be associated with some confidence to the corresponding modes in benzene [33] and are listed as a footnote to Table IV.

TABLE IV. The Vibrational Spectra and the Tentative Assignments of the Series Me_3MCH_2SePh (M = Si, Ge, Sn)[a]

Si		Ge		Sn		Tentative assignments
IR (liq.)	Raman (liq.)	IR (liq.)	Raman (liq.)	IR (liq.)	Raman (liq.)	
2960ms	2950m,dp	2980m	2972m,dp	3000mw	2977m,dp	(a) CH_3(M), CH_2 str.
2910m	2892s,p	2917m	2905s,p	2917m	2908s,p	(s) CH_3(M), CH_2 str.
1410m	1406w,dp	1405w	1396w,dp	1435mw	1430vw,dp	(a) CH_3 def.
1260ms	1264m	1233ms	1236vw,p	1185mw	1186m,p	(s) CH_3 def.
1290w	1284w	1290vw	1288w	1295vw	1291mw	CH_2 def.
1075w	1069m,p	1065w	1063m,p	1070m	1060s,p	X-sen. (q), CH_2 rock
838s	842w	825s	833vw	778ms	783vw	(a) CH_3 rock
750m	753br	730w	734vw	738ms	745vw	(s) CH_3 rock
666ms	672w,p	662w	670mw,p	667w	670w,p	x-sen (r)
690mw	697w,dp	600vs	603m,dp	530s	537m,dp	(a) M–C str.
570w	573m,p	570mw	562vs,p	507ms	510vs,p	(s) M–C str.
460s	462vw	460m	462vw	465w	468vw	X-sen (y)
310w	307mw,p	305vw	307mw,p		307mw,p	X-sen (t)
270s	270mw,dp		185ms,dp	222w	225mw	(a) MC_3 def.
225w	228mw,p		162ms,p		180w	(s) MC_3 def.
	180ms,dp					MC_3 rock

[a] Vibrations associated to the substituent insensitive phenyl modes were observed at: ν(CH) 3062p (z), ν(CC) 1612m,dp (k), 1428vw (m), 1435vw (n), 1328vw (O), β(CH) 1178w,p (a), 1150w,dp (C), 1020m,p (b), ring 995vs,p, ν(CH) 900vw (i), 836vw (g), 738vw (f), α(CCC) 613w,dp (s); ϕ(CC) 400 vvw (W).

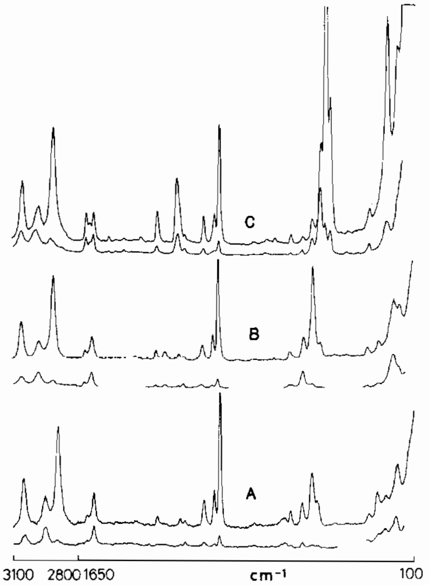

Fig. 4. The Raman spectra of Me_3SiCH_2SePh (A), Me_3Ge-CH_2SePh (B) and Me_3SnCH_2SePh (C).

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References

1 E. W. Abel and D. A. Armitage, *Adv. Organomet. Chem., 5,* 1 (1967).
2 H. Schumann and M. Schmidt, *Angew. Chem., Int. Ed. Engl., 4,* 1007 (1965).
3 M. Lesbre, P. Mazerolles and J. Satge, 'The Organic Compounds of Germanium', Wiley, New York, 1971.
4 D. J. Ayer and R. C. Cookson, *Tetrahedron Lett., 21,* 1967 (1980).
5 F. A. Carey and O. Hernandez, *J. Org. Chem., 38,* 2570 (1973).
6 W. Ehrl and H. Vahrenkamp, *Chem. Ber., 105,* 1471 (1972).
7 K. Sachdev and H. S. Sachdev, *Tetrahedron Lett., 47,* 4223 (1976).
8 E. W. Abel, S. K. Bhargava, K. Kite, K. G. Orrell, V. Sik and B. L. Williams, *Polyhedron, 1,* 289 (1982).
9 E. W. Abel, G. W. Farrow, K. G. Orrell and V. Sik, *J. Chem. Soc., Dalton Trans., 42* (1977).
10 E. W. Abel, A. K. Shamsuddin Ahmed, G. W. Farrow, K. G. Orrell and V. Sik, *J. Chem. Soc., Dalton Trans.,* 47 (1977).
11 J. W. Anderson, G. K. Barker, J. E. Drake and M. Rodger, *J. Chem. Soc., Dalton Trans.,* 1716 (1973).
12 G. K. Barker, J. E. Drake and R. T. Hemmings, *J. Chem. Soc. Dalton Trans.,* 450 (1974).
13 J. E. Drake and R. T. Hemmings, *J. Chem. Soc., Dalton Trans.,* 1730 (1976).
14 J. E. Drake and R. T. Hemmings, *Inorg. Chem., 19,* 1879 (1980).
15 M. Tiecco, L. Testaferri, M. Tingoli, D. Chianelli and M. Montanucci, *Synth. Comm., 13,* 617 (1983).
16 V. F. Mironov, S. A. Mikhailyants and T. K. Gai, *Zh. Obshch. Khim., 39,* 397 (1969).
17 M. Jakoubkova, Z. Papovskava and V. Chvalousky, *Collect. Czech. Chem. Commun., 45,* 854 (1980).
18 D. Seyferth and S. B. Andrews, *J. Organomet. Chem., 30,* 151 (1971).

19 A. L. Allred and E. G. Rochow, *J. Inorg. Nucl. Chem.*, *5*, 269 (1958).
20 R. S. Drago, *J. Inorg. Nucl. Chem.*, *15*, 237 (1960).
21 A. L. Allred and E. G. Rochow, *J. Inorg. Nucl. Chem.*, *20*, 167 (1961).
22 R. W. Taft, Jr., S. Ehrenson, I. C. Lewis and R. E. Glick, *J. Am. Chem. Soc.*, *81*, 5352 (1959).
23 W. McFarlane and R. J. Wood, *J. Chem. Soc., Dalton Trans.*, 1397 (1972).
24 J. R. Allkins and P. J. Hendra, *Spectrochim. Acta, 22*, 2075 (1965); *23*, 1671 (1967).
25 A. L. Smith, *Spectrochim. Acta, 19*, 849 (1953).
26 J. E. Griffiths, *Spectrochim. Acta, 20*, 1335 (1964).
27 J. R. Durig, C. F. Jumper and J. N. Willis, *J. Mol. Spectrosc.*, *37*, 260 (1971).
28 G. Herzberg, 'Infrared and Raman Spectra of Polyatomic Molecules', Van Nostrand, Princeton, N.J., 1945, p. 118.
29 C. V. Stephensen, W. C. Coburn and W. S. Wilcox, *Spectrochim. Acta, 17*, 933 (1961).
30 D. H. Whiffen, *J. Chem. Soc.*, 1350 (1956).
31 D. M. Revitt and D. B. Sowerby, *Spectrochim. Acta, Part A:*, *26*, 1581 (1970).
32 J. H. S. Green and W. Kynaston, *Spectrochim. Acta, Part A:*, *25*, 1677 (1969).
33 R. D. Mair and D. F. Hornig, *J. Chem. Phys.*, *17*, 1236 (1949).
34 F. A. Miller, *J. Chem. Phys.*, *24*, 996 (1956).
35 J. E. Drake, A. Vahradian and B. M. Glavincevski, *Can. J. Chem.*, *61*, 2717 (1983).