Inorganica Chimica Acta, 55 (1981) 171–176
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

Synthesis, Structure and Spectroscopic Studies of Mercury(II) Selenolates and $MeHgSeBu^t$

A. P. ARNOLD and A. J. CANTY*

Chemistry Department, University of Tasmania, Hobart, Tas. 7001 Australia

Received November 11, 1980

Syntheses of Bu^tSeH, $Hg(SeR)_2$ (R = Me, Et, Bu^t), $MeSeHgO_2CMe$, and $MeHgSeBu^t$ are described. The complexes $Hg(SeBu^t)_2$ and $MeSeHgO_2CMe$ have X-ray powder diffraction indicating that they have identical polymeric structures to their thiol analogues. Vibrational spectra for the complex $Hg(SeBu^t)_2$ with tetrahedral coordination for mercury indicate that mercury–selenium stretching modes occur in the region 130–140 cm^{-1}, the linear complex $MeHgSeBu^t$ has ν(Hg–Se) 194 cm^{-1} (IR) [200 cm^{-1} (Raman)] and $J(^1H-^{199}Hg)$ 146.8 Hz, and the other complexes have Hg–Se modes below ca. *200 cm^{-1}.*

Introduction

Selenium has a protective effect in both inorganic [1–3] and methylmercury(II) [2, 4, 5] poisoning. It is of particular interest that for inorganic mercury a direct (chemical) interaction between mercury and a form(s) of selenium *in vivo* appears to be responsible for the protective action of selenium [2, 3]. Little is known about the chemical forms of selenium *in vivo,* although selenoamino acids do occur [1, 6] *e.g.* glycine reductase isolated from *Clostridium sticklandii* contains selenocysteine in the reduced form [7]. Thus, a mercury–selenol interaction may be important in the biological behaviour of mercury. However, the structural chemistry of simple selenolates, $Hg(SeR)_2$, has not been studied, and since we have recently interpreted vibrational spectra of related thiolates $Hg(SR)_2$ (R = Me, Et, Bu^t) [8–10] and $MeSHgO_2CMe$ [11] in terms of established crystal structure determinations [12–15], we have prepared the analogous selenolates and compared their spectroscopic and X-ray powder diffraction data with the thiolates. As this study required preparation of tert-butaneselenol, the MeHg(II) complex of this selenol was also prepared as it is expected to have the lowest value of $J(^1H-^{199}Hg)$ for selenol complexes.

Experimental

Preparation of Selenium Compounds and Complexes

The diselenides R_2Se_2 (R = Me, Et) were prepared as described [16, 17] and purified by distillation [R = Me, b.p. 42–44° (8–9 mm), lit. [18] 43–44° (15 mm); R = Et, b.p. 68–70° (9–10 mm), lit. [18] 74–75° (14 mm)]. As Bu^tSeH has been previously prepared but details of the method not given [19], full details are given here. The complex $Hg(SeMe)_2$ has been prepared by reaction of metallic mercury with Me_2Se_2 [20], and as details of this preparation have not been given they are recorded here; $Hg(SeEt)_2$, which has previously been prepared from mercuric oxide and ethaneselenol [21], was prepared from metallic mercury and Et_2Se_2. The new complex $Hg(SeBu^t)_2$ was prepared from mercuric cyanide and tert-butaneselenol, and the 1:1 complex $MeSeHgO_2CMe$ was prepared following the method reported for $MeSHgO_2CMe$ [22]. $MeHgSBu^t$ was prepared as described [23] [m.p. 40–42 (lit. [23] 41–42°); NMR ($CDCl_3$): δ 0.78 (3H, $MeHg^{II}$), 1.51 (9H, Bu^t), $J(^1H-^{199}Hg)$ 150.1 Hz, lit. ([23] in $CDCl_3$): 0.77, 1.48, 150.2], and $MeHgSeBu^t$ prepared similarly from MeHgOH and Bu^tSeH.

Bis(methaneselenolato)mercury(II)

Excess metallic mercury was stirred with dimethyldiselenide (2.81 g, 15 mmol) in pyridine (50 ml) for 2 days. The resulting yellow and black suspension was extracted with hot pyridine until the extract was colourless (200 ml), the black mercuric selenide and metallic mercury being removed by filtration through cellulose powder and a fine sinter under slight positive pressure. Yellow leaflets of the required product formed on cooling (5.28 g, 90%).

Bis(ethaneselenolato)mercury(II)

Excess metallic mercury was stirred with diethyldiselenide (*ca.* 2 ml, unweighed because of stench) in chloroform (50 ml) for 1 day. The yellow powder which formed was dissolved by addition of hot chloroform (100 ml), and metallic mercury removed by decantation and filtration through a fine sinter

---

*Address enquiries to this author.

under slight positive pressure. Chloroform was removed under vacuum, and the yellow powder recrystallized from pyridine to form yellow prisms of the required product.

Acetato(methaneselenolato)mercury(II), $MeSeHgO_2CMe$

Bis(methaneselenolato)mercury (0.130 g, 0.34 mmol) was added to a solution of mercuric acetate (0.107 g, 0.34 mmol) in water (5 ml) and ethanol (3 ml). After 15 min the colourless solution was filtered to remove a small amount of unreacted $Hg(SeMe)_2$, and the filtrate deposited colourless crystals on slow evaporation. They were collected (0.193 g, 81%) and dried over phosporus pentoxide.

tert-Butaneselenol

Powdered grey selenium (3.83 g, 49 mmol) was added slowly over 30 min with vigorous stirring under nitrogen to a solution of tert-butylmagnesium chloride (prepared from 97 mmol of Bu^tCl) in ether (75 ml). After a further 30 min stirring, ether (50 ml) was added and, after standing for 12 hr, the solution was cooled in ice and ice cold water (50 ml) added. Sulphuric acid (150 ml, 2.5 *M*) was added slowly over a period of 2 hr, and only a small amount of unreacted selenium remained undissolved. The ether layer was separated, the aqueous layer extracted with ether (50 ml), and the combined colourless ether extracts (100 ml) dried over sodium sulphate.

Bis(tert-butaneselenolato)mercury(II)

A portion of the ether extract from preparation of tert-butaneselenol (*ca.* 80 ml) was distilled into a stirred solution of mercuric cyanide (6.12 g, 24 mmol) in methanol (50 ml). The precipitate formed was collected (Whatman No. 1), dissolved in boiling chloroform (250 ml), and on cooling, white needles were collected with a coarse sinter.

tert-Butaneselenolato(methyl)mercury(II)

A portion of the ether extract from preparation of tert-butaneselenol (*ca.* 20 ml) was distilled into an ice-cold solution of MeHgOH [from $MeHgNO_3$ (0.927 g, 3.34 mmol) and NaOH (3 ml, 2 *M*, 6 mmol)] in methanol (40 ml). Water (10 ml) was added, and after standing for 12 hr the solution was filtered through a sinter containing cellulose powder and washed with methanol (20 ml). The solution was extracted twice with hexane (25 ml), NaOH (3 ml, 2 *M*) and water (10 ml) added to the aqueous layer and extracted three more times with hexane (25 ml), and the hexane extracts taken to dryness under low vacuum (*ca.* 25 mm) at 0 °C. The white solid obtained sublimes at 50–60° (15 mm), m. p. 57–58.5° (sealed capillary).

X-ray Powder Diffraction

For $Hg(SeR)_2$ (R = Me, Bu^t) and $MeSeHgO_2CMe$, measured *d* spacings (Å) are given, followed by relative intensities.

$Hg(SeMe)_2$: 8.3 s(br), 6.63 vw, 5.61 w, 4.16 m, 3.90 w, 3.63 m, 3.31 w, 3.17 vw, 3.07 m, 2.90 w, 2.87 w, 2.70 w, 2.66 w, 2.56 m, 2.46 w, 2.42 vw, 2.27 m, 2.22 vw, 2.05 w, 1.96 vw, 1.91 m, 1.87 w, 1.78 vw.

$Hg(SeBu^t)_2$: 9.3 vs(br), 6.45 m(br), 4.84 w, 4.58 w, 4.10 m, 3.89 w, 3.72 w, 3.57 w, 3.19 vw, 3.06 w, 2.91 w, 2.74 m, 2.43 w, 2.30 w, 2.23 w, 2.10 w, 1.84 w, 1.80 w, 1.71 w.

$MeSeHgO_2CMe$: 8.1 s(br), 5.16 w, 4.86 w, 4.15 w, 3.99 w, 3.46 w, 3.21 m, 2.90 vw, 2.65 m(br), 2.49 w, 2.43 vw, 2.31 w, 2.24 vw, 2.21 vw, 2.15 vw, 2.12 vw, 2.05 vw.

Physical Measurements

Infrared spectra (4000–400 cm^{-1}) of complexes in Nujol and hexachlorobutadiene mulls were recorded with a Perkin-Elmer 577 spectrometer. Far IR spectra of complexes in Nujol mulls between polyethylene plates were recorded with a Perkin-Elmer 577 spectrometer (600–200 cm^{-1}) and with a Perkin-Elmer 180 spectrometer (500–100 cm^{-1}) Raman spectra were obtained from powdered samples in sealed capillaries with a Cary 82 laser Raman spectrometer (4000–100 cm^{-1}). For $Hg(SeR)_2$ (R = Me, Et, Bu^t) it was necessary to use a Coherent Radiation Model 1590 dye laser (Rhodamine 6G) as the exciting source to prevent sample decomposition. For R = Et, Bu^t it was also necessary to defocus the laser beam by sample spinning. Direct Ar^+ 514.5 nm excitation was used for the other complexes. Maximum errors are considered to be ±4 cm^{-1} for both IR and Raman spectra.

^1H NMR spectra at 100 MHz were measured on a Jeol-JNM-4H-100 spectrometer. Microanalyses were carried out by Australian Microanalytical Service, Melbourne, and are given in Table I.

Debye-Scherrer X-ray powder diffraction patterns were obtained from powdered complexes in sealed Lindemann tubes using Ni filtered CuKα (λ = 1.5418 Å) or Mn filtered FeKα (λ = 1.9373 Å) radiation.

TABLE I. Analytical Data for the Complexes.

Complex	Found %			Calcd. %		
	C	H	Hg	C	H	Hg
$Hg(SeMe)_2$	6.3	1.5	51.8	6.2	1.6	51.6
$Hg(SeEt)_2$	11.2	2.3	47.7	11.5	2.4	48.2
$Hg(SeBu^t)_2$	20.3	3.9	42.7	20.3	3.8	42.4
$MeSeHgO_2CMe$	10.2	1.7	56.5	10.2	1.7	56.7
$MeHgSeBu^t$	17.0	3.5	57.0	17.1	3.4	57.0

Photographically recorded patterns were measured with a vernier scale, with estimated errors of ±0.1 mm.

Results and Discussion

Reaction of metallic mercury with dialkyldiselenides is a satisfactory preparative method for $Hg(SeR)_2$ (R = Me, Et) (1), $Hg(SeBu^t)_2$ can be prepared from $Hg(CN)_2$ and Bu^tSeH (2), and the complexes $MeSeHgO_2CMe$ (3) and $MeHgSeBu^t$ (4) can be readily obtained by methods suitable for analogous thiolates.

$$Hg + R_2Se_2 \longrightarrow Hg(SeR)_2\ (R = Me, Et) \qquad (1)$$

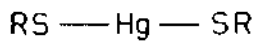
$$Hg(CN)_2 + 2Bu^tSeH \longrightarrow Hg(SeBu^t)_2 + 2HCN \qquad (2)$$

$$Hg(SeMe)_2 + Hg(O_2CMe)_2 \longrightarrow 2MeSeHgO_2CMe \qquad (3)$$

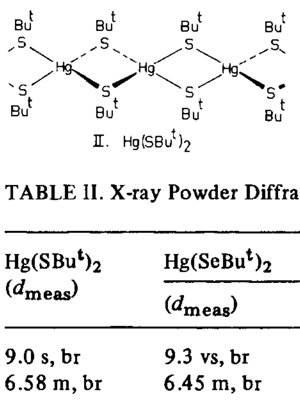
$$MeHgOH + Bu^tSeH \longrightarrow MeHgSeBu^t + H_2O \qquad (4)$$

X-ray Powder Diffraction

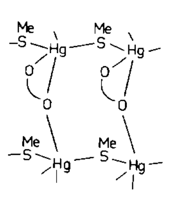
Crystallographic studies reveal that $Hg(SR)_2$ (R = Me [12], Et [13]) are linear molecules (I) with $Hg(SMe)_2$ also having weak intermolecular Hg–S interactions. The complexes $Hg(SBu^t)_2$ [14] and $MeSHgO_2CMe$ [15] are polymeric with bridging sulphur to give tetrahedral 'HgS_4' coordination (II) and a complex coordination geometry 'HgS_2O_3' (III) based on a dominant 'HgS_2' moiety, respectively.



I. R = Me,Et



II. $Hg(SBu^t)_2$



III. $MeSHgO_2CMe$

In addition, $Hg(SMe)_2$ also exists in two crystalline forms, and vibrational spectra establish that the form not studied by single crystal X-ray methods is also linear [10].

X-ray powder photographs of analogous complexes $Hg(XBu^t)_2$ and $MeXHgO_2CMe$ (X = S, Se) are very similar (Table II) indicating that the sulphur and selenium analogues have similar structures. Although some lines of each complex are absent in their analogues, presumably due to the effect of change in scattering between sulphur and selenium (these complexes have 22.3–33.4% Se), spectra of $Hg(SeBu^t)_2$ and $MeSeHgO_2CMe$ may be indexed using unit cell parameters for sulphur analogues, even with the restriction *h*, *k*, and $l \leqslant 4$. The complex $Hg(SeEt)_2$ gives a poor diffraction photograph, showing only diffuse background scattering; and thus X-ray powder diffraction studies establish that $Hg(SeBu^t)_2$ and $MeSeHgO_2CMe$ have structures analogous to II and III but do not reveal the structure of $Hg(SeR)_2$ (R = Me, Et).

Vibrational Spectra

Mercury–sulphur vibrations have been assigned in the ranges 322–216 [11, 24] and 371 (or 405 [8])–172 cm^{-1} [8, 9, 25, 26] for $RSHgO_2CMe$ (R = Me, Et, Pr^n, Bu^n), and 1:2 mercury(II) thiolates, respectively. Complexes $Hg(SR)_2$ (R = Me, Et, Bu^t) have ν(SHgS) modes at frequencies consistent with the expected [27] decrease in frequency with increasing coordination number, *e.g.* $Hg(SMe)_2$ (I) has ν_{as}(SHgS)

TABLE II. X-ray Powder Diffraction Data for $Hg(XBu^t)_2$ and $MeXHgO_2CMe$ (X = S, Se)[a].

$Hg(SBu^t)_2$ (d_{meas})	$Hg(SeBu^t)_2$		$MeSHgO_2CMe$ (d_{meas})	$MeSeHgO_2CMe$	
	(d_{meas})	d_{calc}(hkl)[b]		(d_{meas})	d_{calc}(hkl)[c]
9.0 s, br	9.3 vs, br	9.18 (200)	8.2 s, br	8.1 s, br	8.0 (020)
6.58 m, br	6.45 m, br	6.49 (210)[d]	4.98 m	4.86 w	5.02 (110)
4.54 m	4.58 w	4.59 (020, 400)	4.02 w	3.99 w	3.98 (040), 4.00 (111)
4.15 m	4.10 m	4.11 (220), 4.22 (311)	3.73 m		3.73 (130)
3.97 m	3.89 w	3.92 (021, 401)	3.23 w	3.21 m	3.26 (131), 3.23 (022)
3.03 m	3.06 w	3.03 (312)			3.18 (140)
2.71 w	2.74 m	2.74 (330)	2.64 w	2.65 m, br	2.64 (042), 2.64 (200)
2.32 w	2.30 w	2.30 (040)			2.61 (210)

[a] From powder diffraction using FeKα radiation. Very weak lines are omitted. Very weak lines can also be indexed satisfactorily and *d* spacings for these are given in the Experimental section. [b] Using h, k, l ⩽ 4 and orthorhombic unit cell parameters for $Hg(SBu^t)_2$ [14]. [c] Using h, k, l ⩽ 4 and monoclinic unit cell parameters for $MeSHgO_2CMe$ [15]. [d] However, the reflection (210) is not allowed for space group *C*222.

TABLE III. Vibrational Spectra (600–100 cm^{-1}) for $Hg(XR)_2$ and $MeXHgO_2CMe$ (X = S, Se)^{a}.

$Hg(SMe)_2$ ^{b,c}	$Hg(SeMe)_2$	$Hg(SEt)_2$ ^{c}	$Hg(SeEt)_2$	$Hg(SBu^t)_2$ ^{c}	$Hg(SeBu^t)_2$	$MeSHgO_2CMe$ ^{d}	$MeSeHgO_2CMe$
	578w, sh [576w, sh]						
	570w [572m]^{e}		570vw, sh	573m [579m]			[574s]^{e}
			555m [550m]^{e}				
					514m [519s]^{e}		
						475vw [484w]	477m [480w]
		405s, b^{f,g}		416vw [410m]			
		[*394vs*]^{h,i}			397m		
				377m [382vs]			
337vs^{f} [*338vw*]		332w [335w]		336s [336m]		[377w, sh]	
				322m [322vs]		*322m, b* [*317vw, sh*]^{f}	
296m [*297vs*]^{h}			291w [298w]	292vw [293w]	296w [299m]	[306m]	
		268s, b [245vs]			270w [272w]	[*274vs*]^{h}	
			198w				
204m				[*188vs*]^{h}		[205m]	219m [197w, sh]
[178m]	[182w, sh]		175vs, vb	*172vs, b*^{f}		[171w]	182m [182s]
	161vs, b [158m]	161m [151s]	150vs, vb				
	151vs, b	140m, sh			*135vs* [*139vs, b*]		136s [143s]
	134vs, b [132vs]		130vs [131vs]			[130w]	
110s, vb	103m [112w]		110vs, b	119m			114w, sh

[a] Raman values in parentheses [ ]. Abbreviations: v, very; s, strong; m, medium; w, weak; b, broad; sh, shoulder. [b] 'Old phase', structure determined by X-ray crystallography [12], Fig. 1. [c] From reference 8. [d] From reference 11. [e] ν(CSe). [f] ν_{as}(SHgS). [g] ν_{as}(SHgS) may be 268 cm^{-1} [8]. [h] ν_s(SHgS). [i] ν_s(SHgS) may be 245 cm^{-1} [8].

337 and ν_s 297 cm^{-1} while $Hg(SBu^t)_2$ (II) has ν_{as}(SHgS) 172 and ν_s 188 cm^{-1} [8]. In Table III bands assigned as Hg–S and Hg–Se modes are indicate *in italics*; assignments for $Hg(SR)_2$ (R = Me, Et, Bu^t) and $MeSHgO_2CMe$ are from previous studies.

With the structures of $Hg(SeBu^t)_2$ and $MeSeHgO_2CMe$ established by X-ray powder diffraction, assignment of Hg–Se modes can be attempted by comparison with spectra of thiolates and other complexes containing Hg–Se bonds [28–31], together with the expected [27] decrease in Hg–X modes on replacing sulphur with selenium. Mercury–selenium stretching frequencies for complexes with two-coordinate mercury have been reported to occur in the range 233–178 cm^{-1} [28–31], lower than for Hg–S modes in related complexes, *e.g.* $Se(HgMe)_2$ has ν_{as} 231, ν_s 201 cm^{-1} [29] and $S(HgMe)_2$ has ν_{as} 344, ν_s 300 cm^{-1} [32]; the only 1:2 complex studied, $Hg(SeCF_3)_2$, has ν_{as} 233 (solid mull) and ν_s 178 cm^{-1} (methanol solution) [28]. Tetrahedral mercury in $[Ph_4P]_2[Hg(SePh)_4]$ has ν_s 150 cm^{-1} [30], lower than in $Se(HgMe)_2$ which is assumed to have linear geometry for mercury.

For the selenol complexes described here polymeric structures occur for $Hg(SeBu^t)_2$ and $MeSeHgO_2CMe$, and are possible for $Hg(SeR)_2$ (R = Me, Et). When polymeric structures are possible assignment of metal–ligand modes requires extreme caution, as noted for $[MX_2L_2]_n$ [33] and $MeSHgO_2CMe$ [11, 34], and simple point group approaches are not applicable. Nevertheless, assignment is made below for $Hg(SeBu^t)_2$, and although assignments for the other complexes are not definite the spectra do support earlier assignments of Hg–S modes in the analogous thiolates and suggest that Hg–Se modes occur below *ca.* 200 cm^{-1}.

The tetrahedral complex $Hg(SeBu^t)_2$ has intense bands at 135 (IR), 139 (R) cm^{-1}, and as these are below values observed for Hg–S modes in $Hg(SBu^t)_2$ [172 (IR), 188 (R) cm^{-1}] and similar to ν_s for $[Ph_4P]_2[Hg(SePh)_4]$, they are assigned as Hg–Se modes.

Except for a weak band at 291 (IR) [298 cm^{-1} (Raman)] for $Hg(SeEt)_2$ the complexes $Hg(SeR)_2$ (R = Me, Et) do not have bands in the region 500–200 cm^{-1} where Hg–S modes occur for the sulphur analogues. However, presence of several intense bands in the region 180–100 cm^{-1} in spectra of both complexes indicate that straightforward assignment of Hg–Se modes is not possible.

The 1:1 complex $MeSeHgO_2CMe$ also does not have bands in the region observed for $MeSHgO_2CMe$, but has intense bands at 182 and 136 cm^{-1}, suggesting assignment as Hg–Se modes.

MeHgSeBu^t

The main reason for preparation of $MeHgSeBu^t$ was to obtain the coupling constant $J(^1H–^{199}Hg)$ for the MeHg^{II} group, as it is expected to have a lower coupling constant than any other selenol complex. The coupling constant has been determined for a large number of thiolates [9, 23, 35–38] and a linear correlation is obtained between J(^{1}H–^{199}Hg) and pKa of RSH [37]. The lowest coupling constant obtained is for MeHgSBu^t (150.2 Hz [23]), and as selenol complexes have J(^{1}H–^{199}Hg) lower than their sulphur analogues, *e.g.* MeHgXCH$_2$CH(NH$_3$)CO$_2$ (X = S, 177.2 Hz; X = Se, 164.3 Hz [38], MeHgSeBu^t is expected, and found (146.8 Hz), to have J(^{1}H–^{199}Hg) lower than for other selenolates.

Organomercury(II) thiolates have essentially linear geometry for mercury [39–42] and ν(Hg–S) occurs in the range 388–322 cm^{-1} [9, 25, 41–44], with coincidence of IR and Raman values indicating absence of a centre of symmetry at mercury and thus excluding dimeric structures similar to that found for PhHgOR (R = Me, Et) in the solid state [45]. For MeHgSBu^t and MeHgSeBu^t ν(Hg–C) is readily assigned to bands at 534 m (IR), 536 vs (R) and 521 m (IR), 526 m (R) cm^{-1}, respectively, and ν(Hg–S) at 383 w (IR), 390 m (R) cm^{-1} for MeHgSBu^t. Below 500 cm^{-1} the selenium complex has weak IR absorption at 290 (302 m in Raman) but intense absorption at 194 cm^{-1} (200 s in Raman) readily assigned as ν(Hg–Se) by comparison with two-coordinate mercury in Se(HgMe)$_2$ (ν_{as} 231, ν_s 201 cm^{-1} [29]).

Acknowledgements

We thank the National Health and Medical Research Council for financial support, the Australian Government for a Postgraduate Research Award (A.P.A.), Mr J. C. Bignall of the Central Science Laboratory for assistance with measurement of Raman spectra, and Dr. G. B. Deacon and Mr. M. Hughes for assistance with measurement of IR spectra (500–100 cm^{-1}) at Monash University.

References

1 H. E. Ganther in 'Selenium', R. A. Zingaro and W. C. Cooper (Eds.), Van Nostrand, 1974, p. 546.
2 J. Parizek, *Envir. Health Persp., 25,* 53 (1978) and references therein.
3 M. Berlin, *Envir. Health Persp., 25,* 67 (1978) and references therein.
4 S. Skerfving, *Envir. Health Persp., 25,* 57 (1978) and references therein; H. E. Ganther, *Envir. Health Persp., 25,* 71 (1978) and references therein.
5 R. W. Chen, H. E. Ganther and W. G. Hoekstra, *Biochem. Biophys. Res. Comm., 51,* 383 (1973).
6 M. L. Scott in 'Organic Selenium Compounds. Their Chemistry and Biology', D. L. Klayman and W. H. Gunther (Eds.), Wiley–Interscience, New York, 1973, p. 629.
7 J. E. Cove, R. M. Del Rio and T. C. Stadtman, *J. Biol. Chem., 252,* 5337 (1977).
8 A. J. Canty, R. Kishimoto, G. B. Deacon and G. J. Farquharson, *Inorg. Chim. Acta, 20,* 161 (1976).
9 A. J. Canty and R. Kishimoto, *Inorg. Chim. Acta, 24,* 109 (1977).
10 A. J. Canty and R. K. Tyson, *Inorg. Chim. Acta, 29,* 227 (1978).
11 A. J. Canty, R. Kishimoto and R. K. Tyson, *Aust. J. Chem., 31,* 671 (1978).
12 D. C. Bradley and N. R. Kunchur, *J. Chem. Phys., 40,* 2258 (1964).
13 D. C. Bradley and N. R. Kunchur, *Can. J. Chem., 43,* 2786 (1965).
14 N. R. Kunchur, *Nature, 204,* 468 (1964).
15 A. J. Canty, C. L. Raston and A. H. White, *Aust. J. Chem., 31,* 677 (1978).
16 L. Brandsma and H. E. Wijers, *Rec. Trav. Chim., 82,* 68 (1963).
17 G. M. Bogolybov, Yu-N. Shtyk and A. A. Petrov, *Zh. Obsch. Khim., 39,* 1804 (1969).
18 R. Paetzold, H.-D. Schumann and A. Simon, *Z. Anorg. Allg. Chem., 305,* 96 (1960).
19 R. Gaufrès, A. Perez and J.-L. Bribes, *Bull. Soc. Chim. Fr.,* 2898 (1971).
20 'Beilstein's Handbuch der Organischen Chemie' (4th Edn.), Suppl. Series III, vol. 1, part 1, p. 1220 gives A. Fredga, *Svensk. Kem. Tidskr., 48,* 91 (1936).
21 L. Tschugaeff, *Chem. Ber., 42,* 51 (1909).
22 A. J. Canty and R. K. Tyson, *Inorg. Chim. Acta, 24,* L77 (1977).
23 R. D. Bach and A. T. Weibel, *J. Am. Chem. Soc., 98,* 6241 (1976).
24 H. Puff, R. Sievers and G. Elsner, *Z. Anorg. Allg. Chem., 413,* 37 (1975).
25 N. Iwasaki, J. Tomooka and K. Toyoda, *Bull. Chem. Soc. Jap., 47,* 1323 (1974).
26 P. Biscarini, L. Fusina and G. Nivellini, *J. Chem. Soc. Dalton Trans.,* 2140 (1974).
27 R. J. H. Clark, *Spectrochim. Acta, 21,* 955 (1965).
28 H. J. Chase and E. A. V. Ebsworth, *J. Chem. Soc.,* 940 (1965).
29 D. Breitinger and W. Morell, *Inorg. Nucl. Chem. Lett., 10,* 409 (1974).
30 J. Liesk and G. Klar, *Z. Anorg. Allg. Chem., 435,* 103 (1977).
31 A. J. Carty, S. F. Malone and N. J. Taylor, *J. Organometal Chem., 172,* 201 (1979).
32 N. Iwasaki, *Bull. Chem. Soc. Jap., 49,* 2735 (1976).
33 D. M. Adams and P. J. Lock, *J. Chem. Soc. A,* 620 (1967); M. Goldstein and W. D. Unsworth, *Inorg. Chim. Acta, 4,* 432 (1970); M. Goldstein, *Inorg. Chim. Acta, 31,* L425 (1978); M. Goldstein and R. J. Hughes, *Inorg. Chim. Acta, 37,* 71 (1979).
34 A. J. Canty, *Spectrochim. Acta, Part A, 37,* in press (1981).
35 D. L. Rabenstein, *Accts. Chem. Res., 11,* 100 (1978).
36 R. B. Simpson, *J. Am. Chem. Soc., 83,* 4711 (1961); J. V. Hatton, W. G. Schneider and W. Siebrand, *J. Chem. Phys., 39,* 1330 (1963); R. B. Simpson, *J. Chem. Phys., 46,* 4775 (1967); R. Scheffold, *Helv. Chim. Acta, 50,* 1419 (1967); *52,* 56 (1969); P. G. Simpson, T. E. Hopkins and R. Haque, *J. Phys. Chem., 77,* 2282 (1973); D. L. Rabenstein and M. T. Fairhurst, *J. Am. Chem. Soc., 97,* 2086 (1975); Y. Hojo, Y. Sugiura and H. Tanaka, *J. Inorg. Nucl. Chem., 38,* 641 (1976); P. A. Lampe and P. Moore, *Inorg. Chim. Acta, 36,* 27 (1979); N. W. Alcock, P. A. Lampe and P. Moore, *J. Chem. Soc. Dalton,* 1471 (1980).

37 L. F. Sytsma and R. J. Kline, *J. Organometal. Chem., 54,* 15 (1973).

38 Y. Sugiura, Y. Hojo, Y. Tamai and H. Tanaka, *J. Am. Chem. Soc., 98,* 2339 (1976); Y. Sugiura, Y. Tamai and H. Tanaka, *Bioinorg. Chem., 9,* 167 (1978).

39 L. G. Kuz'mina, N. G. Bokii, Y. T. Struchkov, D. N. Kravstov and E. M. Roklina, *Zh. Strukt. Chim., 15,* 491 (1974); *J. Struct. Chem., 15,* 419 (1974).

40 R. D. Bach, A. T. Weibel, W. Schmonsees and M. D. Glick, *Chem. Comm.,* 961 (1974).

41 N. J. Taylor, Y. S. Wong, P. C. Chieh and A. J. Carty, *J. Chem. Soc. Dalton,* 438 (1975).

42 Y. S. Wong, A. J. Carty and C. Chieh, *J. Chem. Soc. Dalton,* 1801 (1977).

43 R. A. Nyquist and J. R. Mann, *Spectrochim. Acta, Part A, 28,* 511 (1972).

44 A. J. Canty and R. Kishimoto, *Aust. J. Chem., 30,* 669 (1977).

45 A. J. Canty and J. W. Devereux, *Spectrochim. Acta, Part A, 36,* 495 (1980).