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Coordination complexes of triphenyltin coumarin-3-carboxylate with *O*-donor ligands: (coumarin-3-carboxylato)triphenyltin–*L* (*L* = ethanol, diphenylcyclopropenone and quinoline *N*-oxide) and bis[(coumarin-3-carboxylato)triphenyltin]–*L* (*L* = triphenylphosphine oxide and triphenylarsine oxide)

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Abstract

The Sn atoms in (coumarin-3-carboxylato-O^3)(ethanol-O)triphenyltin, [Sn(C$_6$H$_5$)$_3$(C$_{10}$H$_5$O$_4$)(C$_2$H$_6$O)], (coumarin-3-carboxylato-O^3)(1,2-diphenylcyclopropenone-O)triphenyltin, [Sn(C$_6$H$_5$)$_3$(C$_{10}$H$_5$O$_4$)(C$_{15}$H$_{10}$O)], and (coumarin-3-carboxylato-O^3)triphenyl(quinoline N-oxide-O)tin, [Sn(C$_6$H$_5$)$_3$(C$_{10}$H$_5$O$_4$)(C$_9$H$_7$NO)], are five-coordinated with *trans*-C$_3$SnO$_2$ trigonal-bipyramidal geometries. In the ethanol adduct, a hydrogen bond links adjacent molecules into a helical chain along the *b* axis. The molecular 1,2-diphenylcyclopropen-

one and quinoline *N*-oxide adducts were synthesized by condensing triphenyltin hydroxide with coumarin-3-carboxylic acid in ethanol in the presence of an equimolar quantity of the *O*-donor ligand. With triphenylphosphine oxide as the Lewis base, the condensation yields μ-(coumarin-3-carboxylato)-1κO^3:2$\kappa O^{3'}$-(coumarin-3-carboxylato)-1κO^3-hexaphenyl-1$\kappa^3 C$,2$\kappa^3 C$-(triphenylphosphine oxide)-2κO-ditin, [Sn$_2$(C$_6$H$_5$)$_6$(C$_{10}$H$_5$O$_4$)$_2$\{PO(C$_6$H$_5$)$_3$\}]; this dinuclear complex consists of a dimeric carboxylate-bridged bis[(coumarin-3-carboxylato)triphenyltin] entity that is coordinated by the phosphine oxide. μ-(Coumarin-3-carboxylato)-1κO^3:2$\kappa O^{3'}$-(coumarin-3-carboxylato)-1κO^3-hexaphenyl-1$\kappa^3 C$,2$\kappa^3 C$-(triphenylarsine oxide)-2κO-ditin, [Sn$_2$(C$_6$H$_5$)$_6$(C$_{10}$H$_5$O$_4$)$_2$\{AsO(C$_6$H$_5$)$_3$\}], is isomorphous with the phosphine oxide. The carboxylate bridge is longer than the dative Sn—O$_L$ bond in both dinuclear compounds.

Comment

Unlike triorganotin halides and pseudohalides that yield a plethora of 1/1 adducts with 'pointed' (Ng *et al.*, 1982) *O*-donor ligands, triorganotin carboxylates rarely furnish such molecular complexes because the carboxylates are themselves either only weak Lewis acids (as with triphenyltin arylcarboxylates) or are already saturated with respect to coordination through carboxylate bridging (as with triphenyltin alkanoates) (Ng *et al.*, 1988). Complexes of triphenyltin carboxylates with water (Kumar Das *et al.*, 1977; Ng, 1996; Ng & Kumar Das, 1995a; Ng *et al.*, 1996) and methanol (Alcock & Roe, 1989) have been isolated, albeit serendipitously; these adducts are held together in the crystal structure by hydrogen bonds involving the solvate molecules. [Bis(*N*,*N*-dimethylthiocarbamoylthio)acetato]triphenyltin is an unusual example of a triorganotin carboxylate showing Lewis acidity; the compound forms 1/1 complexes with hexamethylphosphoramide, triphenylphosphine oxide (Ng, 1995b) and quinoline *N*-oxide (Ng, 1997). The Lewis acidity of this carboxylate can be attributed to the electron-withdrawing capacity of the dimethylthiocarbamoylthiolyl units in the anionic group; in fact, the compound is so Lewis acidic that even ethanol can coordinate to it (Ng & Kumar Das, 1991). On the other hand, bis(triphenyltin) succinate, which yields isolable adducts with several *O*-donor ligands (Ng, 1998a), represents an anomaly, as the succinato group is not normally considered a strongly basic entity.

Although the coumarin-3-carboxylate anion does not appear to be able to endow the triphenyltin derivative with enhanced Lewis acidity, triphenyltin coumarin-3-carboxylate accepts a coumarin-3-carboxylate anion to form the bis(coumarin-3-carboxylato)triphenylstannate anion, which has been structurally characterized as its tetramethylammonium salt (Ng & Kumar Das, 1997b).

The geometry of the Sn atom in this salt is similar to that found for the Sn atom in bis(trifluoroacetato)triphenylstannate (Ng, 1998b; Ng & Kumar Das, 1997a). The isolation of the former stannate implies that the parent carboxylate must therefore possess Lewis acidity comparable with that of triphenyltin trifluoroacetate, whose acceptor strength can be attributed to the trifluoromethyl unit in the anionic group.

Triphenyltin coumarin-3-carboxylate, when synthesized by condensing triphenyltin hydroxide with coumarin-3-carboxylic acid in toluene, exists as a hydrate. The water molecule in this compound is probably coordinated to the Sn atom; it is expected to form hydrogen bonds to the carbonyl groups of the anion. In the ethanol complex, (I), the coumarin unit is perfectly planar (r.m.s. deviation 0.011 Å); the carboxyl group is twisted with respect to this plane by 43.6 (8)° so that its carboxyl O atom can form a short hydrogen bond [2.629 (8) Å] with the ethanol O atom. The dative Sn—O bond distance is similar to that [2.394 (8) Å] found in the ethanol adduct of 2-triphenylstannyl-1,2-benzisothiazol-3(2H)-one 1,1-dioxide (Ng et al., 1989), as well as that [2.465 (4) Å] found in bis(dicyclohexylammonium) tris(oxalato)tetrakis(tributylstannate)–2ethanol (Ng et al., 1990).

(I)

(II)

(III)

(IV)

(V)
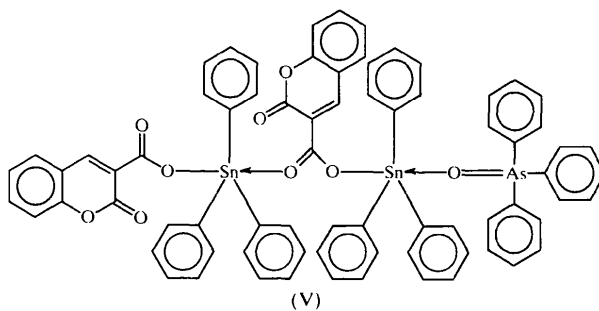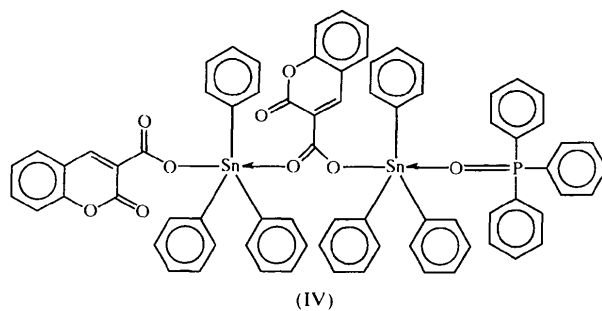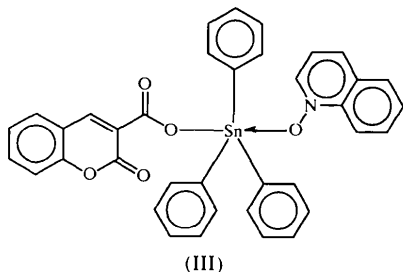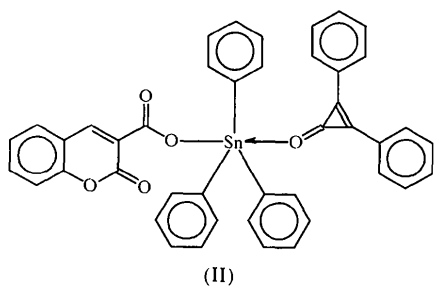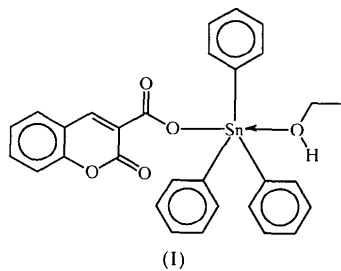
Although 1,2-diphenylcyclopropenone is a stronger Lewis base compared with ethanol arising from the ability of the cyclopropene ring to disperse the positive charge, the Sn—O bond distance in the triphenyltin coumarin-3-carboxylate adduct, (II), is nevertheless not much different from that in the ethanol adduct. The Sn—O distance is similar to that [2.540 (2) Å] found in chlorotriphenyltin–1,2-diphenycyclopropenone (Ng & Kumar Das, 1993). Replacing the ketone donor by an N-oxide results in an adduct, (III), having a dative Sn—O bond [2.407 (2) Å] that is shorter than that in (II) but longer than that in (I). This distance is similar to that [2.446 (4) Å] found in the [bis(N,N-dimethylthiocarbamoylthio)acetato]triphenyltin adduct (Ng, 1997). The Sn—O—E angles in (II) [138.0 (5)°] and (III) [121.9 (2)°] imply an sp^2 type of hybridization at the O atom.

The reaction between stoichiometric amounts of triphenyltin coumarin-3-carboxylate and triphenylphosphine oxide furnishes a dinuclear bis(triphenyltin coumarin-3-carboxylate), (IV), having only one of its monomeric units (molecule b) coordinated by the Lewis base. As this moiety uses its doubly bonded carboxyl O atom to bond to the other monomeric unit (molecule a), the dinuclear adduct represents an example of a triorganotin carboxylate that exhibits both Lewis acidic as well as Lewis basic character in one molecule. A similar feature has also been observed in both the hexanuclear complex [bis(triphenyltin) succinate]–2(quinoline N-oxide) (Ng & Kumar Das, 1995b) and bis(triphenyltin 3-oxapentamethylenethiocarbamoyl-S-acetate) hydrate (Ng, 1996); in the latter, the donor ligand is a water molecule that links the dimers into a chain. Coordination by the phosphine
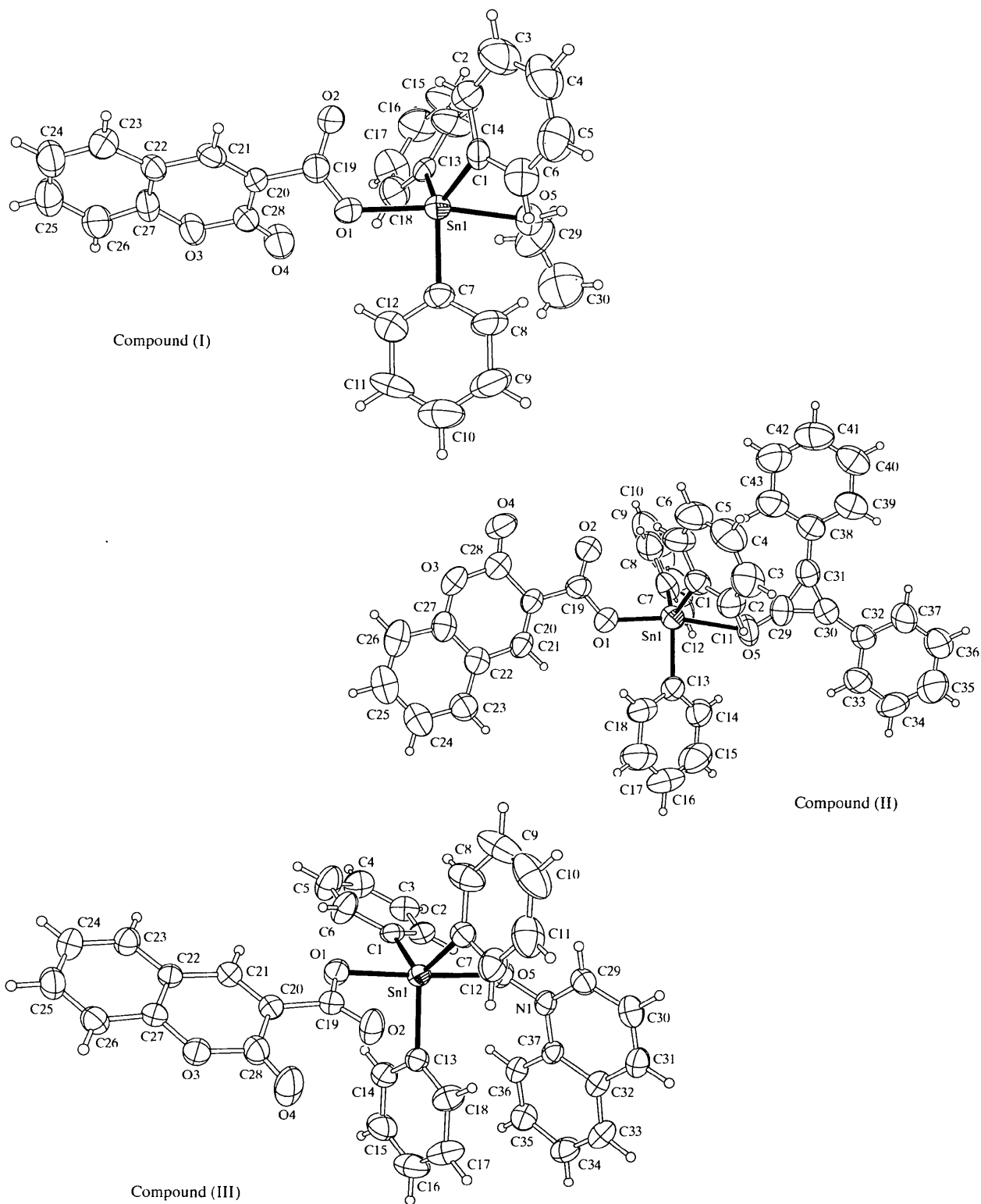
Fig. 1. *ORTEP*II (Johnson, 1976) plots of compounds (I), (II) and (III) at the 50% probability level. H atoms are drawn as spheres of arbitrary radii.

oxide to the Sn atom of molecule *b* [Sn—O(phosphine oxide) = 2.369 (3) Å and O—Sn—O = 172.8 (1)°] weakens the carboxylate bridge that links molecule *a* [Sn—O(carboxylate bridge) = 2.514 (3) Å and O—Sn—O = 168.1 (1)°] to molecule *b*. The Sn—O—P angle [166.4 (2) Å], which is the among the largest for the

phosphine oxide complexes of inorganic and organotin halides (Ng, 1995*a*; Ng & Kumar Das, 1992, 1996; Rheingold *et al.*, 1984), reflects the crowding of the phosphine oxide when it coordinates to molecule *b*.

The triphenylarsine analog, (V), is isomorphous. The Sn—O(arsine oxide) distance [2.260 (3) Å] is shorter
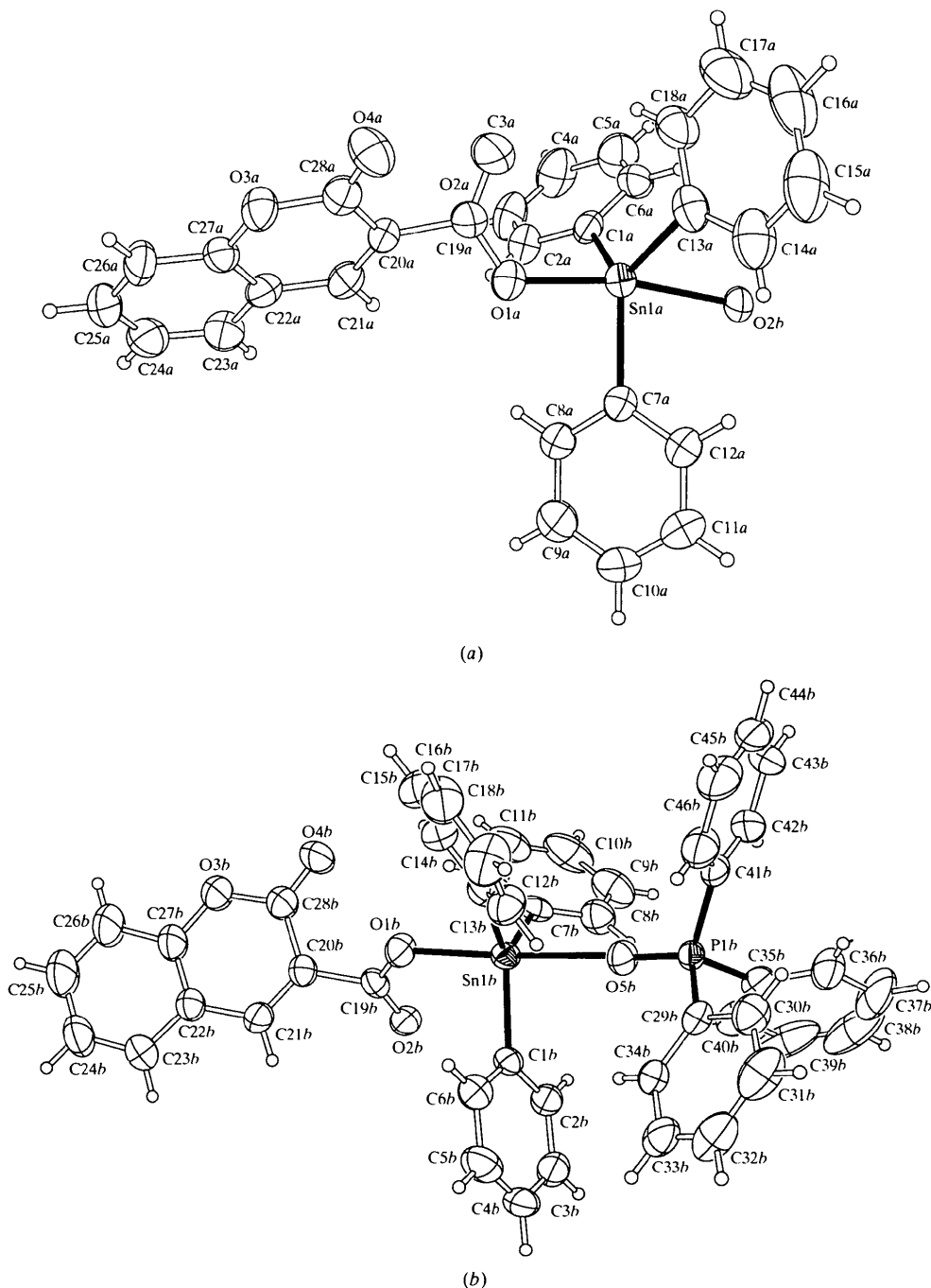

(a)

(b)

Fig. 2. *ORTEP*II (Johnson, 1976) plots of (a) the (coumarin-3-carboxylato)triphenyltin molecule and (b) the (coumarin-3-carboxylato)triphenyltin–triphenylphosphine oxide molecule of (IV) at the 50% probability level. H atoms are drawn as spheres of arbitrary radii.

than that in the phosphine oxide adduct; however, because the arsenic–oxygen bond [1.647 (3) Å] is much longer than the phosphorus–oxygen bond [1.492 (3) Å], there is less crowding at molecule b, so that the Sn—O—As skeleton is more bent [Sn—O—As = 159.4 (2)°].

Experimental

Equimolar amounts of triphenyltin hydroxide and coumarin-3-carboxylic acid were heated in a small volume of 95%

ethanol. The filtered solution when cooled afforded crystals of the ethanol adduct (I) [m.p. 417–418 K (decomposition)]. Analysis found: C 61.30, H 4.16%; calculated for $C_{30}H_{26}O_5Sn$: C 61.57, H 4.48%; Sn^{119m} Mössbauer (80 K): isomer shift (IS) = 1.25, quadrupole splitting (QS) = 3.20, τ_1 = 1.13, τ_2 = 1.10 mm s^{-1}; IR (Nujol): –CO_2 1738, 1635, 1605, 1568 cm^{-1} (cf. 1741 cm^{-1} for the carbonyl stretch in coumarin-3-carboxylic acid). An attempt to synthesize the ethanol-free compound by carrying out the reaction in toluene in a Dean–Stark water separator gave instead the hydrated compound, aqua(coumarin-3-carboxylato)triphenyltin, which
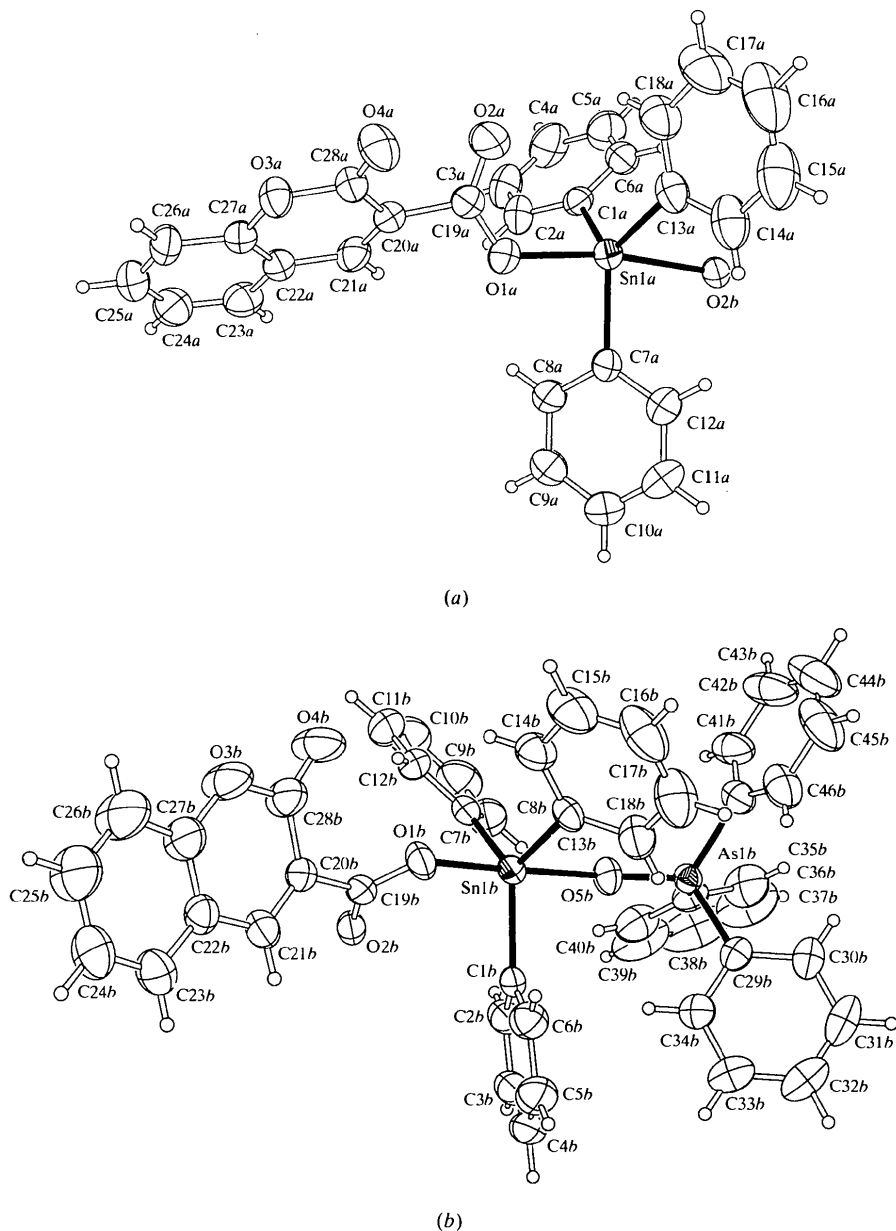

(a)

(b)

Fig. 3. ORTEPII (Johnson, 1976) plots of (a) the (coumarin-3-carboxylato)triphenyltin molecule and (b) the (coumarin-3-carboxylato)triphenyltin–triphenylarsine oxide molecule of (V) at the 50% probability level. H atoms are drawn as spheres of arbitrary radii.

was purified from chloroform to give a white powder that failed to yield crystals. Analysis found: C 60.50, H 3.60%; calculated for $C_{28}H_{22}O_5Sn$: C 60.36, H 3.98%; Sn^{119m} Mössbauer: IS = 1.27, QS = 3.53, τ_1 = 1.03, τ_2 = 1.13 mm s^{-1}.

The 1,2-diphenylcyclopropenone adduct, (II), was synthesized by heating equimolar amounts of triphenyltin hydroxide, coumarin-3-carboxylic acid and 1,2-diphenylcyclopropenone in ethanol. Slow cooling of the filtered mixture afforded crystals of (II) (m.p. 412–414 K). Analysis found: C 69.30, H 3.95%; calculated for $C_{43}H_{30}O_5Sn$: C 69.71, H 5.85%; Sn^{119m} Mössbauer: IS = 1.23, QS = 3.14, τ_1 = 1.31, τ_2 = 1.28 mm s^{-1}; IR: $-CO_2/CO$ 1731, 1660 1607, 1588, 1566 cm^{-1}.

Condensation in the presence of an equimolar amount of quinoline N-oxide hydrate gave the analogous amine–oxide complex (III) (m.p. 434–435 K). Analysis found: C 64.60, H 3.92%; calculated for $C_{37}H_{27}NO_5Sn$: C 64.94, H 3.98%; Sn^{119m} Mössbauer: IS = 1.20, QS = 2.95, τ_1 = 1.10, τ_2 = 1.07 mm s^{-1}; IR: $-CO_2$ 1751, 1637, 1608, 1567; N → O 1275 cm^{-1}.

The condensation was performed with an equimolar amount of triphenylphosphine oxide to afford complex (IV) (m.p. 443–444 K). Analysis found: C 65.70, H 4.08%; calculated for $C_{74}H_{55}O_9PSn_2$: C 65.52; H 4.09%; Sn^{119m} Mössbauer: IS = 1.24, QS = 3.25, τ_1 = 1.06, τ_2 = 1.05 mm s^{-1}; IR: $-CO_2$ 1752, 1646, 1582; P → O 1272 cm^{-1}.

The analogous reaction with an equimolar amount of triphenylarsine oxide produced complex (V) (m.p. 443–446 K). Analysis found: C 63.50, H 3.91%; calculated for $C_{74}H_{55}$-AsO_9Sn_2: C 63.46, H 3.96%; Sn^{119m} Mössbauer: IS = 1.20, QS = 3.14, τ_1 = 1.14, τ_2 = 1.12 mm s^{-1}; IR: $-CO_2$ 1743, 1608, 1569; As → O 877 cm^{-1}.

Compound (I)

Crystal data

[$Sn(C_6H_5)_3(C_{10}H_5O_4)$-
(C_2H_6O)]
M_r = 585.20
Monoclinic
$P2_1/c$
a = 9.115 (2) Å
b = 14.226 (2) Å
c = 20.224 (4) Å
β = 93.532 (9)°
V = 2617.6 (8) Å^3
Z = 4
D_x = 1.485 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 8.0–10.0°
μ = 1.014 mm^{-1}
T = 298 (2) K
Plate
0.22 × 0.22 × 0.11 mm
Colorless

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction:
ψ scan (North et al., 1968)
T_{min} = 0.852, T_{max} = 0.897
3651 measured reflections
3398 independent reflections

2244 reflections with
$I > 2\sigma(I)$
R_{int} = 0.038
θ_{max} = 22.44°
h = 0 → 9
k = 0 → 15
l = −21 → 21
3 standard reflections
frequency: 60 min
intensity decay: 4%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.052
$wR(F^2)$ = 0.118
S = 0.992
3398 reflections
289 parameters
H atoms riding; U(H) = 1.5U_{eq}(C,O)

$w = 1/[\sigma^2(F_o^2) + (0.0500P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.395 e Å^{-3}
$\Delta\rho_{min}$ = −0.552 e Å^{-3}
Extinction correction: none
Scattering factors from
International Tables for
Crystallography (Vol. C)

Table 1. Selected geometric parameters (Å, °) for (I)

Sn1—C1	2.129 (4)	Sn1—O1	2.147 (5)
Sn1—C7	2.135 (4)	Sn1—O5	2.401 (5)
Sn1—C13	2.120 (4)		
C1—Sn1—C13	114.1 (2)	C7—Sn1—O1	87.1 (2)
C1—Sn1—C7	117.5 (2)	C7—Sn1—O5	85.9 (2)
C1—Sn1—O1	107.2 (2)	C13—Sn1—O1	93.1 (2)
C1—Sn1—O5	86.0 (2)	C13—Sn1—O5	81.9 (2)
C7—Sn1—C13	125.7 (2)	O1—Sn1—O5	166.8 (2)

Compound (II)

Crystal data

[$Sn(C_6H_5)_3(C_{10}H_5O_4)$-
$(C_{15}H_{10}O)$]
M_r = 745.36
Monoclinic
$P2_1/n$
a = 12.712 (2) Å
b = 19.402 (2) Å
c = 14.456 (3) Å
β = 97.242 (9)°
V = 3536.8 (9) Å^3
Z = 4
D_x = 1.400 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 8.0–10.0°
μ = 0.767 mm^{-1}
T = 298 (2) K
Block
0.36 × 0.32 × 0.28 mm
Colorless

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction:
ψ scan (North et al., 1968)
T_{min} = 0.720, T_{max} = 0.814
6519 measured reflections
6224 independent reflections

3496 reflections with
$I > 2\sigma(I)$
R_{int} = 0.049
θ_{max} = 25°
h = 0 → 15
k = 0 → 23
l = −17 → 17
3 standard reflections
frequency: 60 min
intensity decay: 3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.059
$wR(F^2)$ = 0.126
S = 0.989
6224 reflections
382 parameters
H atoms riding; U(H) = 1.5U_{eq}(C)

$w = 1/[\sigma^2(F_o^2) + (0.0446P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.321 e Å^{-3}
$\Delta\rho_{min}$ = −0.291 e Å^{-3}
Extinction correction: none
Scattering factors from
International Tables for
Crystallography (Vol. C)

Table 2. *Selected geometric parameters (Å, °) for (II)*

Sn1—C1	2.130 (3)	Sn1—O1	2.107 (4)
Sn1—C7	2.130 (4)	Sn1—O5	2.425 (4)
Sn1—C13	2.135 (4)		
C1—Sn1—C7	120.7 (2)	C7—Sn1—O1	101.4 (2)
C1—Sn1—C13	117.6 (2)	C7—Sn1—O5	85.5 (2)
C1—Sn1—O1	96.7 (2)	C13—Sn1—O1	87.5 (2)
C1—Sn1—O5	87.3 (2)	C13—Sn1—O5	81.3 (2)
C7—Sn1—C13	119.2 (2)	O1—Sn1—O5	168.8 (2)

Compound (III)

Crystal data

[Sn(C$_6$H$_5$)$_3$(C$_{10}$H$_5$O$_4$)-
 (C$_9$H$_7$NO)]
M_r = 684.29
Triclinic
$P\bar{1}$
a = 10.4099 (3) Å
b = 11.520 (1) Å
c = 13.725 (2) Å
α = 111.754 (8)°
β = 95.758 (7)°
γ = 98.695 (5)°
V = 1489.0 (2) Å^3
Z = 2
D_x = 1.526 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25
 reflections
θ = 8.0–10.0°
μ = 0.905 mm^{-1}
T = 298 (2) K
Block
0.29 × 0.29 × 0.29 mm
Colorless

Data collection

Enraf–Nonius CAD-4
 diffractometer
ω–2θ scans
Absorption correction:
 ψ scan (North *et al.*,
 1968)
 T_{min} = 0.712, T_{max} = 0.779
5562 measured reflections
5241 independent reflections

4564 reflections with
 $I > 2\sigma(I)$
R_{int} = 0.018
θ_{max} = 25.01°
h = 0 → 12
k = −13 → 13
l = −16 → 16
3 standard reflections
 frequency: 60 min
 intensity decay: 10%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.080
S = 1.013
5241 reflections
361 parameters
H atoms riding; U(H) =
 1.5U_{eq}(C)

w = 1/[$\sigma^2(F_o^2)$ + (0.0436P)^2
 + 0.5665P]
 where P = (F_o^2 + 2F_c^2)/3
(Δ/σ)$_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.337 e Å^{-3}
$\Delta\rho_{min}$ = −0.503 e Å^{-3}
Extinction correction: none
Scattering factors from
 *International Tables for
 Crystallography* (Vol. C)

Table 3. *Selected geometric parameters (Å, °) for (III)*

Sn1—C1	2.160 (2)	Sn1—O1	2.163 (2)
Sn1—C7	2.136 (2)	Sn1—O5	2.407 (2)
Sn1—C13	2.129 (2)		
C1—Sn1—C7	120.4 (1)	C7—Sn1—O1	97.1 (1)
C1—Sn1—C13	112.7 (1)	C7—Sn1—O5	85.9 (1)
C1—Sn1—O1	91.3 (1)	C13—Sn1—O1	94.1 (1)
C1—Sn1—O5	83.5 (1)	C13—Sn1—O5	87.7 (1)
C7—Sn1—C13	125.2 (1)	O1—Sn1—O5	174.8 (1)

Compound (IV)

Crystal data

[Sn$_2$(C$_6$H$_5$)$_6$(C$_{10}$H$_5$O$_4$)$_2$-
 (C$_{18}$H$_{15}$OP)]
M_r = 1356.53
Triclinic
$P\bar{1}$
a = 9.4696 (6) Å
b = 16.164 (2) Å
c = 20.816 (2) Å
α = 79.329 (8)°
β = 81.946 (7)°
γ = 80.861 (7)°
V = 3071.1 (5) Å^3
Z = 2
D_x = 1.467 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25
 reflections
θ = 12.0–13.0°
μ = 0.899 mm^{-1}
T = 298 (2) K
Block
0.36 × 0.32 × 0.28 mm
Colorless

Data collection

Enraf–Nonius CAD-4
 diffractometer
ω–θ scans
Absorption correction:
 ψ scan (North *et al.*,
 1968)
 T_{min} = 0.737, T_{max} = 0.787
10 759 measured reflections
10 759 independent
 reflections

8333 reflections with
 $I > 2\sigma(I)$
θ_{max} = 24.96°
h = 0 → 11
k = −18 → 19
l = −24 → 24
3 standard reflections
 frequency: 60 min
 intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.102
S = 1.069
10 759 reflections
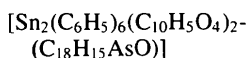667 parameters
H atoms riding; U(H) =
 1.5U_{eq}(C)

w = 1/[$\sigma^2(F_o^2)$ + (0.0266P)^2
 + 5.4654P]
 where P = (F_o^2 + 2F_c^2)/3
(Δ/σ)$_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.444 e Å^{-3}
$\Delta\rho_{min}$ = −0.384 e Å^{-3}
Extinction correction: none
Scattering factors from
 *International Tables for
 Crystallography* (Vol. C)

Table 4. *Selected geometric parameters (Å, °) for (IV)*

Sn1a—C1a	2.132 (3)	Sn1b—C13b	2.141 (3)
Sn1a—C13a	2.130 (3)	Sn1b—O1b	2.143 (3)
Sn1a—C7a	2.135 (3)	Sn1b—O5b	2.369 (3)
Sn1a—O1a	2.118 (3)	P1b—C29b	1.804 (3)
Sn1a—O2b	2.514 (3)	P1b—C35b	1.789 (3)
Sn1b—C1b	2.128 (2)	P1b—C41b	1.792 (3)
Sn1b—C7b	2.139 (3)	P1b—O5b	1.492 (3)
C1a—Sn1a—C7a	120.2 (1)	C7b—Sn1b—C13b	117.1 (1)
C1a—Sn1a—C13a	113.5 (1)	C7b—Sn1b—O1b	95.6 (1)
C1a—Sn1a—O1a	94.9 (1)	C7b—Sn1b—O5b	89.6 (1)
C1a—Sn1a—O2b	83.7 (1)	C13b—Sn1b—O1b	85.1 (1)
C7a—Sn1a—C13a	122.8 (2)	O1b—Sn1b—O5b	172.8 (1)
C7a—Sn1a—O1a	88.2 (1)	C13b—Sn1b—O5b	88.1 (1)
C7a—Sn1a—O2b	82.3 (1)	C29b—P1b—C41b	108.9 (2)
C13a—Sn1a—O1a	105.9 (2)	C29b—P1b—C35b	103.7 (2)
C13a—Sn1a—O2b	85.4 (1)	C29b—P1b—O5b	111.7 (2)
O1a—Sn1a—O2b	168.1 (1)	C35b—P1b—C41b	107.0 (2)
C1b—Sn1b—C7b	124.0 (1)	C35b—P1b—O5b	110.8 (2)
C1b—Sn1b—C13b	118.5 (1)	C41b—P1b—O5b	114.1 (2)
C1b—Sn1b—O1b	95.6 (1)	P1b—O5b—Sn1b	166.4 (2)
C1b—Sn1b—O5b	85.5 (1)		

Compound (V)

Crystal data

$[Sn_2(C_6H_5)_6(C_{10}H_5O_4)_2$-
$(C_{18}H_{15}AsO)]$
$M_r = 1400.48$
Triclinic
$P\bar{1}$
$a = 9.5242\ (4)$ Å
$b = 16.219\ (2)$ Å
$c = 20.807\ (2)$ Å
$\alpha = 79.501\ (9)°$
$\beta = 81.793\ (7)°$
$\gamma = 80.523\ (6)°$
$V = 3096.0\ (5)$ Å^3
$Z = 2$
$D_x = 1.502$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25
reflections
$\theta = 12.0–13.0°$
$\mu = 1.396$ mm^{-1}
$T = 298\ (2)$ K
Block
$0.40 \times 0.40 \times 0.40$ mm
Colorless

Data collection

Enraf–Nonius CAD-4
diffractometer
$\omega–\theta$ scans
Absorption correction:
ψ scan (North et al.,
1968)
$T_{min} = 0.545$, $T_{max} = 0.572$
10 851 measured reflections
10 851 independent
reflections

8629 reflections with
$I > 2\sigma(I)$
$\theta_{max} = 24.96°$
$h = 0 \rightarrow 11$
$k = -18 \rightarrow 19$
$l = -24 \rightarrow 24$
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.093$
$S = 1.085$
10 851 reflections
667 parameters
H atoms riding; U(H) =
$1.5U_{eq}$(C)

$w = 1/[\sigma^2(F_o^2) + (0.0327P)^2$
$+ 3.7829P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.424$ e Å^{-3}
$\Delta\rho_{min} = -0.357$ e Å^{-3}
Extinction correction: none
Scattering factors from
International Tables for
Crystallography (Vol. C)

Table 5. Selected geometric parameters (Å, °) for (V)

Sn1a—C1a	2.132 (2)	Sn1b—C13b	2.141 (2)
Sn1a—C7a	2.136 (2)	Sn1b—O1b	2.170 (3)
Sn1a—C13a	2.126 (3)	Sn1b—O5b	2.260 (3)
Sn1a—O1a	2.123 (3)	As1b—O5b	1.647 (3)
Sn1a—O2b	2.479 (3)	As1b—C29b	1.903 (2)
Sn1b—C1b	2.130 (2)	As1b—C35b	1.889 (3)
Sn1b—C7b	2.138 (3)	As1b—C41b	1.893 (3)
C1a—Sn1a—C7a	119.8 (1)	C7b—Sn1b—C13b	117.9 (1)
C1a—Sn1a—C13a	113.5 (1)	C7b—Sn1b—O1b	94.4 (1)
C1a—Sn1a—O1a	94.6 (1)	C7b—Sn1b—O5b	88.7 (1)
C1a—Sn1a—O2b	84.5 (1)	C13b—Sn1b—O1b	83.9 (1)
C7a—Sn1a—C13a	123.5 (1)	C13b—Sn1b—O5b	91.3 (1)
C7a—Sn1a—O1a	88.1 (1)	O1b—Sn1b—O5b	175.1 (1)
C7a—Sn1a—O2b	82.6 (1)	C29b—As1b—C41b	109.6 (2)
C13a—Sn1a—O2b	85.2 (1)	C29b—As1b—C35b	104.7 (2)
C13a—Sn1a—O1a	105.4 (1)	C29b—As1b—O5b	111.0 (2)
O1a—Sn1a—O2b	168.6 (1)	C35b—As1b—C41b	106.8 (2)
C1b—Sn1b—C7b	124.4 (1)	C35b—As1b—O5b	108.7 (2)
C1b—Sn1b—C13b	117.6 (1)	C41b—As1b—O5b	115.4 (2)
C1b—Sn1b—O1b	94.0 (1)	As1b—O5b—Sn1b	159.4 (2)
C1b—Sn1b—O5b	87.3 (1)		

The phenyl rings in the structures were refined as rigid hexagons.

For all compounds, data collection: *CAD-4 VAX/PC* (Enraf–Nonius, 1988); cell refinement: *CELDIM* in *CAD-4 VAX/PC*; data reduction: *MolEN* (Fair, 1990) and *XCAD-4* (Harms, 1997); program(s) used to solve structures: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structures: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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Monooxovanadium(V) complexes with bidentate *N*-phenylbenzohydroxamate

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Abstract

Two complexes of oxovanadium(V) with VO(ONO)-(OO)-type coordination were synthesized and analysed by X-ray diffraction. These compounds are (acetylacetone benzoylhydrazonato-O,N,O')(*N*-hydroxy-*N*-phenylbenzamido-O,O')oxovanadium(V), [VO($C_{12}H_{12}N_2O_2$)($C_{13}H_{10}NO_2$)], and (*N*-hydroxy-*N*-phenylbenzamido-O,O')oxo(*N*-salicylidene-L-alaninato-O,N,O')vanadium(V), [VO($C_{10}H_9NO_3$)($C_{13}H_{10}NO_2$)]; *N*-hydroxy-*N*-phenylbenzamide is also known as *N*-phenylbenzohydroxamic acid. The distorted octahedral coordination at vanadium is similar in both complexes; the equatorial plane is defined by one N and two O atoms of the tridentate hydrazone ligand and the oxime O atom of the hydroxamate ligand, while the axial oxo group is *trans* to the carbonyl O atom of the hydroxamate ligand.

Comment

The presence of hydroxamic acids at the active sites of some biological enzymes (Kurzak *et al.*, 1992) and the discovery of the biological relevance of hydroxamato–vanadium complexes (Cornman *et al.*, 1992) have resulted in increased interest in the study of their structural properties. However, only a few structures of the simplest vanadium complexes with hydroxamate ligands have been reported (Cornman *et al.*, 1992; Fisher *et al.*, 1989; Pecoraro, 1989; Gibney *et al.*, 1993; Liu & Gao, 1998, 1999).

As part of a continuing study of oxovanadium–hydroxamate complexes, we report the syntheses and structures of (acetylacetone benzoylhydrazonato-O,N,O')oxo(*N*-phenylbenzohydroxamato-O,O')vanadium(V), (1), and oxo(*N*-phenylbenzohydroxamate-O,O')(*N*-salicylidene-L-alaninato-O,N,O')vanadium(V), (2). The coordination geometry and bond parameters of

(1) and (2) are similar to those in [VOL^1(bbz)] and [VOL^2(bbz)]·CH_3OH [where H_2L^1 is *N*-salicylideneglycine, H_2L^2 is *N*-(2-carboxyphenyl)salicylidenamine and H_2bbz is *N*-phenylbenzohydroxamic acid; Liu & Gao, 1999].

(1)   (2)
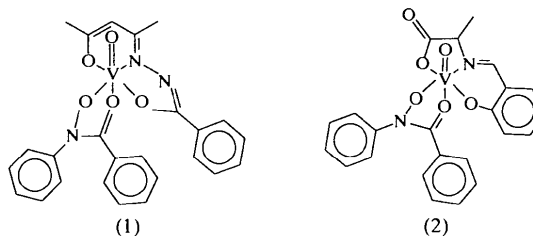
In both compounds, the atom *trans* to the oxo O atom is the carbonyl O atom of the hydroxamate ligand. The *trans* axial angle is 167.05 (8)° in complex (1), and 171.6 (2) and 173.6 (2)° in complex (2). The axial V—O bonds (*trans* to V=O) are longer than the equatorial V—O bonds due to the structural *trans* effect. The oxo–vanadium bond lengths range from 1.573 (3) to 1.589 (3) Å, which are within the range of most V—O bond distances.

Compound (2) crystallizes in the polar space group $P2_1$ with two molecules in the asymmetric unit. This is similar to its chiral precursor, aquaoxo(*N*-salicylidene-L-alaninato)vanadium [(IV); Hämäläinen *et al.*, 1985]. The preparation of the complex does not influence the stereochemistry at the chiral C8 and C8' atoms. Although the two independent molecules appear to be related by a centre of inversion, as would occur if the space group were $P2_1/n$, refinement in this centrosymmetric space group would not converge. Careful examination of the stereochemistry at the chiral C atoms shows that both chiral centres (C8 and C8') have the
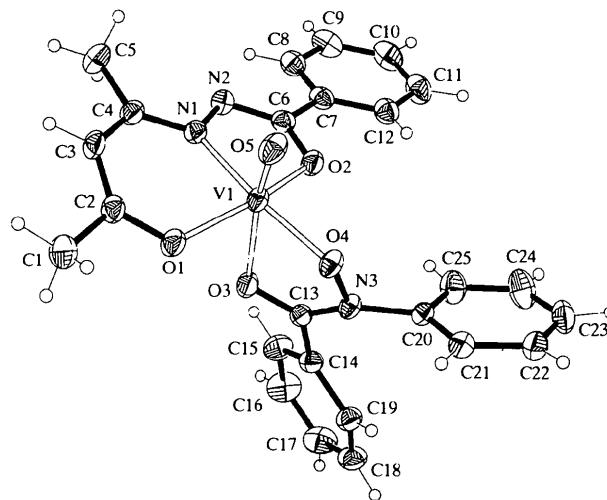

Fig. 1. *ORTEP*II (Johnson, 1976) plot for (1) drawn at the 30% probability level. H atoms are drawn as spheres of arbitrary radii.