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Triorganoantimony(V) complexes with internally functionallized oximes: synthetic, spectroscopic and structural aspects of [$R_3Sb(Br)L$], [$R_3Sb(OH)L$] and [R_3SbL_2], crystal and molecular structures of [$Me_3Sb\{ON{=}C(Me)C_4H_3O\}_2$], [$Me_3Sb\{ON{=}C(Me)C_4H_3S\}_2$], 2-$OC_4H_3C(Me){=}NOH$ and 2-$SC_4H_3C(Me){=}NOH$

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Abstract

Triorganoantimony(V) complexes with internally functionallized oximes of the type [$R_3Sb\{ON{=}C(Me)Ar\}_2$] (**1**) [R = Me, Pr^i; Ar = C_5H_4N, C_4H_3S, C_4H_3O] have been prepared by the reaction of R_3SbBr_2 with the corresponding oximes in 1:2 molar ratio in anhydrous benzene. Treatment of **1** with one equivalent of R_3SbX_2 afforded a redistribution product [$R_3Sb(X)\{ON{=}C(Me)Ar\}$] (**2**) [X = (**a**):Br, (**b**):OH]. The species, $R_3Sb(OH)L$, may also be obtained by the controlled hydrolysis of **1** (R = Pr^i; Ar = C_5H_4N). All of these complexes have been characterized by elemental analyses, and IR and NMR (^1H and ^{13}C) spectroscopic studies. Crystal structures of [$Me_3Sb\{ON{=}C(Me)C_4H_3O\text{-}2\}_2$] (**3**), [$Me_3Sb\{ON{=}C(Me)C_4H_3S\text{-}2\}_2$] (**4**) 2-$OC_4H_3C(Me){=}NOH$ (**5**) and 2-$SC_4H_3C(Me){=}NOH$ (**6**) are reported. The geometry around the antimony atom in **3** and **4** is distorted trigonal bipyramidal with the carbon atoms of the $SbMe_3$ unit in equatorial positions and the two oxygen atoms of the oxime group occupying axial positions (O(1)–Sb–O(2) 171.67(12) in **3** and 169.14(13) in **4**). The free oxime is clearly hydrogen bonded (H–N 2.08 Å in **6**) to essentially form a dimer. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Trialkylantimony(V); Oximes; NMR; X-ray

1. Introduction

The chemistry of organoantimony(V) complexes has attracted considerable attention during the last two decades or so [1–4]. These complexes show wide structural diversity from monomeric molecular species, to associated structures and supramolecular assemblies [5–9]. In addition, several organoantimony compounds exhibited antimicrobial properties [10] as well as antitumor activities [11,12]. The biological toxicity of organoantimony derivatives is much less than those of Pt and Pd anticancer substances [13,14].

Among multidentate organic ligands, oximes are known to have biological functions [15–17] such as growth regulatory, antimicrobial and fungicidal activities. The oxime groups are also present in the althiomycin antibiotic molecule [18]. There are relatively few reports of organoantimony(V) oximates [9,19–21]. The trialkylantimony(V) derivatives, [$R_3Sb\{ON{=}C(Me)R'\}_2$], are volatile under reduced pressure [21], whereas the corresponding triaryl derivatives, [Ph_3Sb-

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{ON=C(Me)R′}$_2$], decompose to Ph_3Sb and oximes under similar conditions [20]. More recently [9] crystal structures of [Ph_4Sb{ON=C(CN)C(O)NH_2] and [Ph_4Sb{ON=C(CN)C(O)N(CH_3)$_2$] have been reported in which the cynooxime anions are bound to the antimony(V) atom in a monodentate fashion via the oxygen atom of the oxime group.

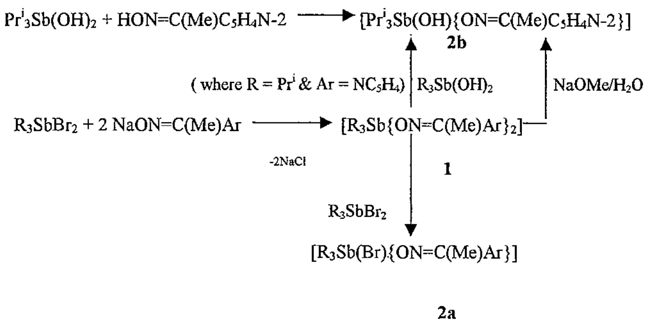
However, corresponding triorganoantimony(V) compounds with internally functionallized oximes such as 2-heteroaryl methyl ketone oximes, are hitherto unknown. The 2-heteroaryl methyl ketone oximes may exist in two isomeric forms *E* and *Z*. Our attempts to prepare *Z*-oximes in which the heteroatom at the two position may act as the coordination site led us to the synthesis of *E*-isomer, as confirmed by crystal structure analyses of 2-acetylfuran ketoxime and 2-acetylthiophene ketoxime.

In view of the above it was considered to be worthwhile to investigate the chemistry of a series of organoantimony(V) complexes with internally functionallized oximes. In these cases there may be an opportunity to combine useful properties related to the organometallic nature of the molecule with those of the acido-oxime ligand. This could be of importance in designing a new group of organoantimony compounds with potentially useful anticancer properties.

2. Results and discussion

2.1. Preparation

All reactions were carried out in strictly anhydrous conditions under inert atmosphere and monitored by ^{1}H-NMR spectroscopy. The reaction of R_3SbBr_2 with the sodium salt of 2-heteroaryl methyl ketone oximes in 1:2 stoichiometry in refluxing anhydrous benzene readily gives [R_3Sb{ON=C(Me)Ar}$_2$] (**1**) [R = Me, Pr^i.; Ar = C_5H_4N, C_4H_3E (E = O, S)]. The latter, on treatment with one equivalent of R_3SbBr_2, affords the redistribution products [R_3Sb(Br){ON=C(Me)Ar}] (**2a**). The reactions are quite facile and can be shown by ^{1}H-NMR spectroscopy to be completed immediately at room temperature. However, the corresponding redistribution reaction involving [Pr^i_3Sb{ON=C(Me)C_5H_4N-2}$_2$] and [$Pr^i_3Sb(OH)_2$] is rather slow and takes several days to reach completion. Thus, the ^{1}H-NMR spectrum of a freshly prepared solution of a 1:1 mixture of [Pr^i_3Sb{ON=C(Me)C_5H_4N-2}$_2$] and [$Pr^i_3Sb(OH)_2$] in $CDCl_3$ shows resonances attributable to these starting materials. After a few minutes, resonances attributable to [Pr^i_3Sb(OH){ON=C(Me)C_5H_4N-2}] appear and, with time, their intensity increases with a concomitant decrease in the intensity of the resonances of the starting materials. After 4 days, the resonances attributable to the hydroxo species, [Pr^i_3Sb(OH){ON=C(Me)C_5H_4N-2}] predominate (~ 90%). This complex can also be prepared by the reaction of [$Pr^i_3Sb(OH)_2$] with free oxime in 1:1 molar ratio or by the partial hydrolysis of [Pr^i_3Sb{ON=C(Me)C_5H_4N-2}$_2$] (Scheme 1). It is worth noting that the complexes [R_3Sb(Br)(O_2PPh_2)] establish an equilibrium in solution with R_3SbBr_2 and [$R_3Sb(O_2PPh_2)_2$] [8]. All the complexes are colorless crystalline solids or pastes and are soluble in common organic solvents.



Scheme 1.

2.2. IR and NMR spectra

The IR spectra of these complexes were interpreted by comparison with those of the free oximes, R_3SbBr_2, (R = Me, Pr^i), [$Pr^i_3Sb(OH)_2$] and other related complexes [22]. A medium to strong intensity band in the region 495–568 cm^{-1} has been attributed to ν Sb–C, while a weak to medium intensity band in the region 307–350 cm^{-1} has been assigned to ν Sb–O [20,21]. The ^{1}H and ^{13}C{^{1}H}-NMR spectra of these complexes exhibited characteristic peaks and peak multiplicities for R–Sb and ligand protons as well as for carbon atoms. The data are summarized in Table 1. The Sb–Me and CH–Sb proton and carbon resonances for Me_3Sb and Pr^i_3Sb complexes are shielded on substituting bromine with oximate in R_3SbBr_2. The shielding of these resonances increases in the order: $R_3SbBr_2 < R_3SbBrL < R_3SbL_2$. These resonances for a given series (i.e. **1** or **2a** and **2b**) are not influenced to any degree by the nature of oxime. The ligand proton resonances on coordination with antimony show no significant changes in chemical shift, except for the methyl signal which, in general, appears at higher field than that for the corresponding free oxime. In the ^{13}C-NMR spectra of triorganoantimony(V) complexes, C-2 and C=N in general are deshielded as compared to their positions for the corresponding free ligands. However, other resonances are essentially unchanged indicating that the heteroatom of the aryl group is not coordinated to antimony. This is further substantiated by the X-ray structures of **3** and **4**.

Table 1
^{1}H and $^{13}C\{^{1}H\}$-NMR data for oximes and their triorganoantimony(V) complexes in $CDCl_3$

Complexes	$^{13}C\{^{1}H\}$-NMR δ in ppm	^{1}H-NMR δ in ppm
$2\text{-}NC_5H_4C(Me)$=NOH	10.7 (Me); 120.6 (C-5); 123.4 (C-3); 136.3 (C-4); 148.8 (C-6); 154.6 (C-2); 156.5 (C=N)	2.44 (s, Me); 7.25 (td, 1.1 Hz (d), 6.1 Hz (t), H-4); 7.68 (td, 1.8 Hz (d), 8 Hz (t), H-5); 7.83 (dt, 0.9 Hz (t), 8 Hz (d), H-3); 8.63 (m, H-6); 9.08 (br, s, OH)
$[Me_3SbBr_2]$	26.7 (Sb–Me)	2.63 (s, Sb–Me)
$[Me_3Sb\{ON{=}C(Me)C_5H_4N\}_2]$	5.7 (Sb–Me); 10.2 (oxime–Me); 119.8 (C-5); 122.5 (C-3); 135.6 (C-4); 148.6 (C-6); 156.4 (C-2); 156.8 (C=N)	1.75 (s, Sb–Me); 2.27 (s, oxime–Me); 7.18 (dt, 1 Hz (d), 2.5 Hz (t), H-4); 7.63 (dt, 1.8 Hz (d), 6 Hz (t), H-5); 7.92 (d, 8 Hz, H-3); 8.57 (d, 4 Hz, H-6)
$[Me_3Sb(Br)\{ON{=}C(Me)C_5H_4N\}]$	10.3 (oxime–Me); 16.6 (Sb–Me); 119.9 (C-5); 123.0 (C-3); 135.8 (C-4); 148.8 (C-6); 155.2 (C-2); 158.5 (C=N)	2.23 (s, Sb–Me); 2.26 (s, oxime–Me); 7.25 (t, 3 Hz, H-4); 7.65 (t, 8 Hz, H-5); 7.81 (d, 8 Hz, H-3); 8.57 (d, 6 Hz, H-6)
$[Pr^i_3SbBr_2]$	21.4 (Sb–CHMe_2); 52.7 (Sb–C)	1.63 (d, 7 Hz, Sb–CHMe_2); 3.45 (sep, 7 Hz, Sb–CH)
$[Pr^i_3Sb\{ON{=}C(Me)C_5H_4N\}_2]$	10.1 (oxime–Me); 20.8 (Sb–CHMe_2); 35.7 (Sb–C); 119.5 (C-5); 122.2 (C-3); 135.7 (C-4); 148.6 (C-6); 156.2 (C-2); 156.7 (C=N)	1.59 (d, 7.3 Hz, SbCHMe_2); 2.31 (s, oxime–Me); 3.05 (sep, 7.3 Hz, SbCH$<$); 7.15 (dd, 1.2 Hz each, H-4); 7.60 (t, 1 Hz, H-5); 7.95 (d, 8 Hz, H-3); 8.56 (d, 4 Hz, H-6)
$[Pr^i_3Sb(Br)\{ON{=}C(Me)C_5H_4N\}]$	10.1 (oxime–Me); 20.7 (Sb–CHMe_2); 44.2 (Sb–C); 119.4 (C-5); 122.7 (C-3); 135.7 (C-4); 148.6 (C-6); 155.5 (C-2); 158.2 (C=N)	1.56 (d, 7.2 Hz, Sb–CHMe_2); 2.27 (s, oxime–Me); 3.15 (sep, 7.2 Hz, SbCH$<$); 7.16 (dd, 1.3 Hz, 5 Hz, H-4); 7.60 (t, 8 Hz, H-5); 7.82 (d, 8 Hz, H-3); 8.53 (d, 4 Hz, H-6)
$[Pr^i_3Sb(OH)_2]$	20.2 (Sb–CHMe_2); 36.2 (Sb–C)	0.28 (s, OH); 1.47 (d, 7.3 Hz, Sb–CHMe_2); 2.43 (sep, 7.3 Hz, SbCH$<$)
$[Pr^i_3Sb(OH)\{ON{=}C(Me)C_5H_4N\}]$	10.0 (oxime–Me); 20.7 (Sb–CHMe_2); 35.1 (Sb–C); 119.3 (C-5); 121.9 (C-3); 135.4 (C-4); 148.5 (C-6); 155.7 (C-2); 157.1 (C=N)	0.39 (s, OH); 1.51 (d, 7.3 Hz, Sb–CHMe_2); 2.26 (s, oxime–Me); 2.78 (sep, 7.3 Hz, SbCH$<$); 7.15 (dd, H-4); 7.62 (t, H-5); 7.90 (d, H-3); 8.55 (d, H-6)
$2\text{-}OC_4H_3C(Me)$=NOH	11.0 (C–Me); 109.6 (C-4); 111.2 (C-3); 143.5 (C-5); 147.6 (C-2); 150.3 (C=N)	2.21 (s, Me); 6.42 (d,d, 1.6 Hz each, H-4); 6.62 (d, 3.4 Hz, H-3); 7.45 (br, H-5); 9.82 (br, s, OH)
$[Me_3Sb\{ON{=}C(Me)C_4H_3O\}_2]$	5.6 (Sb–Me); 10.9 (oxime–Me); 106.8 (C-4); 111.0 (C-3); 142.2 (C-5); 148.0 (C-2); 152.7 (C=N)	1.72 (s, Sb–Me); 2.08 (s, oxime–Me); 6.41 (t, 1.5 Hz, H-4); 6.51 (d, 2.4 Hz, H-3); 7.42 (s, C-5)
$[Me_3Sb(Br)\{ON{=}C(Me)C_4H_3O\}]$	10.9 (oxime–Me); 16.6 (Sb–Me); 108.1 (C-4); 111.1 (C-3); 142.8 (C-5); 149.7 (C-2); 151.4 (C=N)	2.07 (s, oxime–Me); 2.21 (s, Sb–Me); 6.41 (br, H-4); 6.54 (br, H-3); 7.42 (br, s, H-5)
$[Pr^i_3Sb\{ON{=}C(Me)C_4H_3O\}_2]$	10.6 (oxime–Me); 20.7 (Sb–CHMe_2); 35.9 (Sb–C); 105.8 (C-4); 111.0 (C-3); 141.9 (C-5); 147.4 (C-2); 153.4 (C=N)	1.60 (d, 7.3 Hz, Sb–CHMe_2); 2.16 (s, oxime–Me); 3.01 (sep, 7.3 Hz, SbCH$<$); 6.42 (m, H-4); 6.53 (d, 3.4 Hz, H-3); 7.42 (br, s, H-5)
$[Pr^i_3Sb(Br)\{ON{=}C(Me)C_4H_3O\}]$	10.7 (oxime–Me); 20.7 (Sb–CHMe_2); 44.5 (Sb–C); 107.2 (C-4); 111.1 (C-3); 142.6 (C-5); 149.2 (C-2); 151.9 (C=N)	1.59 (d, 7.2 Hz, Sb–CHMe_2); 2.11 (s, oxime–Me); 3.16 (sep, 7.3 Hz, SbCH$<$); 6.41 (m, H-4); 6.52 (d, 3.3 Hz, H-3); 7.41 (br, s, H-5)
$2\text{-}SC_4H_3C(Me)$=NOH	12.3 (C–Me); 126.3 (C-4); 126.7 (C-3); 127.0 (C-5); 140.4 (C-2); 151.8 (C=N)	2.38 (s, Me);7.13 (m, H-4); 7.35 (d, H-3); 7.64 (d, H-5); 8.01 (b, OH)
$[Me_3Sb\{ON{=}C(Me)C_4H_3S\}_2]$	5.7 (Sb–Me); 11.7 (oxime–Me); 123.9 (C-4); 125.1 (C-3); 126.7 (C-5); 143.4 (C-2); 150.8 (C=N)	1.74 (s, Sb–Me); 2.19 (s, oxime–Me); 7.01 (dd, 4.5 Hz, H-4); 7.19 (d, 3.2 Hz, H-3); 7.18 (d, 5 Hz, H-5)
$[Me_3Sb(Br)\{ON{=}C(Me)C_4H_3S\}]$	11.8 (oxime–Me); 16.7 (Sb–Me); 125.1 (C-4); 126.0 (C-3); 126.9 (C-5); 141.8 (C-2); 152.6 (C=N)	2.13 (s, oxime–Me); 2.18 (Sb–Me); 6.90 (br, H-4); 7.13 (br, H-3); 7.20 (br, H-5)

2.3. X-ray crystal structures of $[Me_3Sb\{ON{=}C(Me)C_4H_3O\text{-}2\}_2]$ (**3**), $Me_3Sb\{ON{=}C(Me)C_4H_3S\text{-}2\}_2]$ (**4**), $2\text{-}OC_4H_3C(Me){=}NOH$ (**5**) and $2\text{-}SC_4H_3C(Me){=}NOH$ (**6**)

Important experimental parameters in the X-ray structural analyses of **3**–**6** are given in Table 2. The molecular structures of **3**–**6**, with the atom numbering schemes, are shown in Figs. 1–3, and selected interatomic distances and angles are listed in Tables 3 and 4. $[Me_3Sb\{ON{=}C(Me)C_4H_3O\text{-}2\}_2]$ (**3**) and $[Me_3Sb\{ON{=}C(Me)C_4H_3S\text{-}2\}_2]$ (**4**) exhibit similar trigonal bipyramidal monomeric structures with no intermolecular interactions. Two oxime moieties are coordinated to the central antimony atom with the two oxygen atoms occupying axial positions [O(1)–Sb(1)–O(3) 171.67(12)E for **3** and O(1)–Sb(1)–O(2) 169.14(13)E for **4**]. The carbon atoms of the $SbMe_3$ unit in the equatorial positions have C–Sb(1)–C angles ranging from 116.0(2) to 123(2)E. Their sum, as expected for a planar moiety, is 360E in both molecules. The average Sb–O bond of 2.087(5) Å is slightly longer than the sum of the covalent radii of Sb and O (2.07 Å), while the average Sb–C bond of 2.098(5) Å is slightly shorter than the sum of the covalent radii of Sb and C (2.18 Å), as expected for the axial and equatorial positions of a trigonal bipyramid. The interatomic distances from antimony to the oxygen or sulphur atoms of the $2\text{-}OC_4H_3$ or $2\text{-}SC_4H_3$

moieties are 5.239(4) and 5.094(4) Å for Sb(1)–O(2) and Sb(1)–O(4), respectively, in **3** and 5.346(4) and 5.096(4) Å for Sb(1)–S(1) and Sb(1)–S(2), respectively, in **4**. These distances are well outside the sum of the van der Waals radii of Sb and O or Sb and S, thus confirming that the unidentate linkage of the oximes that was indicated by the NMR spectra of solutions is found in the solid state. A comparison of the bond lengths in the free oximes and those bonded to antimony indicates that there are no significant differences. The N–O distances in 2-$OC_4H_3C(Me)$=NOH (5) [average N–O bond length for the three molecules in the asymmetric unit is 1.414(8) Å] and in 2-$SC_4H_3C(Me)$=NOH (6) [1.4071(16) Å] are only marginally longer than those in **3** [average 1.395(2) Å] and **4** [average 1.392(3) Å], while the C–N distances in **5** [average C–N bond length for the three molecules in the asymmetric unit is 1.30(5) Å] and **6** [1.282(2) Å] are essentially the same as in **3** [average 1.301(12) Å] and **4** [average 1.280(2) Å], respectively. The distinguishing features of the rings of the bonded and free oxime ligands are of course the result of the differences in the bonds and angles involving the O or S atoms. Thus the C–O distances average 1.375(27) in **5** and 1.370(9) Å in **3** with C–O–C angles of 105.6(13) and 107.0(5)°, respectively, while the C–S distances average 1.717(11) in **6** and 1.696(8) Å in **4** with C–S–C angles of 91.99(8) and 91.8(3)°, respectively. The hydrogen bonding in 2-$SC_4H_3C(Me)$=NOH (**6**), which essentially results in a dimer, is depicted in Fig. 4. The H(1)–N(1)N distance is 2.08(2), the O(1)–N(1)N distance 2.7986(19) Å and the O(1)–H(1)–N(1)N angle 156(2)°. The H atom attached to oxygen was found in the difference map for only one of the molecules in the asymmetric unit of 2-$OC_4H_3C(Me)$=NOH (**5**). The corresponding distances and angles are H(1)–N(1)O, 1.85(6), O(1)–N(1)O, 2.796(6) Å and O(1)–H(1)–N(1)O, 159(5)°. In the other two molecules the closest intermolecular O–N distances are 2.776(7) and 2.793(6) Å.

Table 2
Crystal data and structure refinement parameters for [$Me_3Sb\{ON{=}C(Me)C_4H_3O\text{-}2\}_2$] (**3**), [$Me_3Sb\{ON{=}C(Me)C_4H_3S\text{-}2\}_2$] (**4**), 2-$OC_4H_3C(Me)$=NOH (**5**) and 2-$SC_4H_3C(Me)$=NOH (**6**)

Compound	3	4	5	6
Empirical formula	$C_{15}H_{21}N_2O_4Sb$	$C_{15}H_{21}N_2O_2S_2Sb$	$C_6H_7NO_2$	C_6H_7NOS
Formula weight	415.09	447.21	125.13	141.19
Temperature (°C)	−123(2)	−123(2)	−123(2)	−123(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Trigonal	Monoclinic
Space group	$P2_1/c$	$P2_1/n$	$P3_2$	$P2_1/c$
Unit cell dimensions				
a (Å)	9.2483(18)	9.5274(19)	14.016(2)	8.392(2)
b (Å)	16.647(3)	9.2500(19)	14.016(2)	14.802(3)
c (Å)	11.998(2)	21.723(4)	8.1524(16)	5.6209(11)
α (°)	90	90	90	90
β (°)	108.04(3)	102.43(3)	90	106.78(3).
γ (°)	90	90	120	90
V (Å^3)	1756.3(6)	1869.5(7)	1387.0(4)	668.5(2)
Z	4	4	9	4
D_{calc} (g cm^{-3})	1.570	1.589	1.348	1.403
Absorption coefficient (mm^{-1})	1.588	1.706	0.102	0.393
F(000)	832	896	594	296
Crystal size (mm)	0.10×0.03×0.02	0.25×0.20×0.20	0.20×0.10×0.10	0.40×0.25×0.22
θ range for data collection (°)	3.03 to 27.44	2.92 to 27.53	3.01 to 27.50	3.74 to 27.47
Index ranges	$-11\leq h\leq 11$, $-21\leq k\leq 21$, $-15\leq l\leq 15$	$-12\leq h\leq 11$, $-11\leq k\leq 11$, $-27\leq l\leq 28$	$-18\leq h\leq 14$, $-16\leq k\leq 18$, $-8\leq l\leq 10$	$-10\leq h\leq 10$, $-19\leq k\leq 16$, $-7\leq l\leq 6$
Reflections collected	13468	10413	5876	4114
Independent reflections	3989 [$R_{int}=0.1477$]	3739 [$R_{int}=0.0552$]	3350 [$R_{int}=0.0502$]	1500 [$R_{int}=0.0303$]
Max/min transmission	0.9689, 0.8573	0.7299, 0.6750	0.9898, 0.9798	0.9184, 0.8585
Refinement method	Full-matrix least-squares on F^2			
Data/restraints/parameters	3989/0/205	3739/0/205	3350/1/257	1500/0/110
Final R indices [$F^2>4\sigma(F^2)$]	$R_1=0.0519$, $wR_2=0.1025$	$R_1=0.0425$, $wR_2=0.1069$	$R_1=0.0585$, $wR_2=0.1286$	$R_1=0.0330$, $wR_2=0.0803$
R indices (all data)	$R_1=0.0931$, $wR_2=0.1164$	$R_1=0.0665$, $wR_2=0.1192$	$R_1=0.0859$, $wR_2=0.1424$	$R_1=0.0389$, $wR_2=0.0838$
Extinction coefficient	0.0006(5)	0.0027(7)		0.009(7)
Goodness-of-fit on F^2	0.967	1.024	1.039	1.042
Largest difference peak and hole (e Å^{-3})	1.042 and −1.960	0.747 and −0.731	0.554 and −0.247	0.268 and −0.271

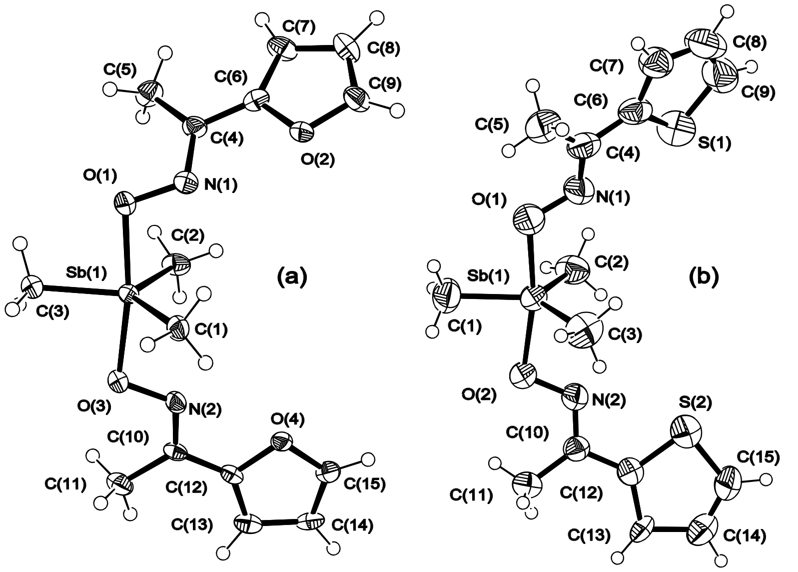


Fig. 1. ORTEP plot of the molecules (a) $[Me_3Sb\{ON{=}C(Me)C_4H_3O\text{-}2\}_2]$ (**3**) and (b) $[Me_3Sb\{ON{=}C(Me)C_4H_3S\text{-}2\}_2]$ (**4**). The atoms are drawn with 50% probability ellipsoids.

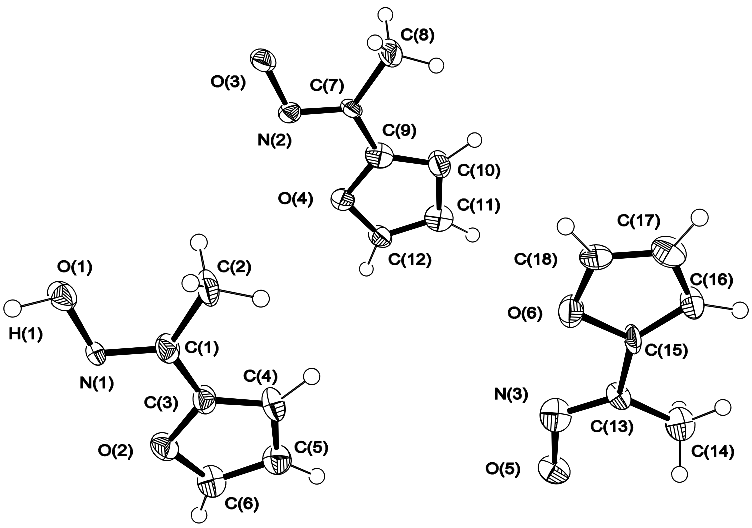


Fig. 2. ORTEP plot of the three independent molecules in the asymmetric unit of $2\text{-}OC_4H_3C(Me){=}NOH$ (**5**). The atoms are drawn with 50% probability ellipsoids.

3. Experimental

2-Acetylpyridine, 2-acetylfuran, 2-acetylthiophene were obtained from Sisco-Chem. Oximes [23], Me_3SbBr_2 [24] and $Pr^i_3SbBr_2$ [25] were prepared according to literature methods. All reactions were carried out in anhydrous solvents unless stated otherwise. IR spectra were recorded as Nujol mulls between CsI plates in a Bomen MB-102 FT IR spectrometer. ^1H and $^{13}C\{^1H\}$-NMR spectra were recorded in 5 mm NMR tubes as freshly prepared $CDCl_3$ solutions in a Bruker DPX-300 spectrometer operating at 300 and 75.47 MHz, respectively. Spectra were referenced with internal chloroform peak (*7.26 for ^1H and 77.0 for ^{13}C).

3.1. Preparation of $[Pr^i_3Sb(OH)_2]$

To a stirred benzene solution (25 ml) of $Pr^i_3SbBr_2$ (4.335 g, 10.55 mmol) methanolic solution of sodium methoxide [prepared from sodium metal (501 mg, 21.78 mmol) in MeOH] was added. The whole was stirred with refluxing for 3 h. After cooling to room temperature (r.t.), 0.4 ml distilled water was added and further stirred for 30 min. The solvents were evaporated under vacuum and the residue was extracted with benzene (10×2 ml) and filtered. The filtrate was concentrated in vacuo and the residue was recrystallized from CH_2Cl_2 at − 10EC as colorless crystals (yield 2.564 g, 85%). IR: 3396 (ν OH); 495 (ν Sb–C); 305 (ν Sb–O).

3.2. Preparation of [$Me_3Sb\{ON{=}C(Me)C_5H_4N\text{-}2\}_2$]

To a methanolic solution of sodium salt of 2-acetylpyridyl oxime [prepared from sodium metal (127 mg, 5.52 mmol) dissolved in MeOH (15 ml) and 2-acetylpyridine ketoxime (752 mg, 5.52 mmol)] a benzene suspension (20 ml) of Me_3SbBr_2 (902 mg, 2.76 mmol) was added with vigorous stirring. The reactants were refluxed for 4 h. The solvents were evaporated under vacuum and the residue was extracted with benzene (15 × 2 ml) and filtered through G-3 filtration unit. The solvent was stripped off in vacuo to give a colorless paste. This was recrystallized from hexane at −10EC as colorless crystals (yield 996 mg, 82%). Similarly all other [$R_3Sb\{ON{=}C(Me)Ar\}_2$] complexes were prepared. Pertinent data are summarized in Table 5.

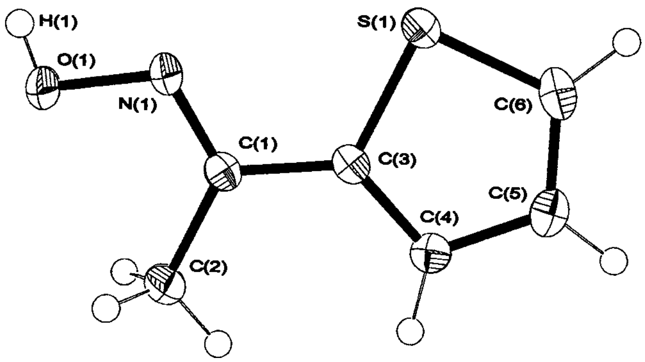


Fig. 3. ORTEP plot of the molecule 2-$SC_4H_3C(Me){=}NOH$ (**6**). The atoms are drawn with 50% probability ellipsoids.

Table 3
Selected bond lengths (Å) and bond angles (°) for [$Me_3Sb\{ON{=}C(Me)C_4H_3O\text{-}2\}_2$] (**3**) and [$Me_3Sb\{ON{=}C(Me)C_4H_3S\text{-}2\}_2$] (**4**)

3		**4**	
Bond lengths			
Sb(1)–C(1)	2.102(5)	Sb(1)–C(1)	2.095(5)
Sb(1)–C(2)	2.105(5)	Sb(1)–C(2)	2.093(5)
Sb(1)–C(3)	2.096(5)	Sb(1)–C(3)	2.096(6)
Sb(1)–O(1)	2.088(3)	Sb(1)–O(1)	2.091(3)
Sb(1)–O(3)	2.088(3)	Sb(1)–O(2)	2.079(3)
O(1)–N(1)	1.396(5)	O(1)–N(1)	1.394(5)
N(1)–C(4)	1.310(6)	N(1)–C(4)	1.282(6)
C(4)–C(5)	1.481(7)	C(4)–C(5)	1.477(7)
C(4)–C(6)	1.448(7)	C(4)–C(6)	1.487(8)
C(6)–C(7)	1.359(7)	C(6)–C(7)	1.379(7)
C(7)–C(8)	1.423(7)	C(7)–C(8)	1.377(8)
C(8)–C(9)	1.347(7)	C(8)–C(9)	1.338(9)
O(2)–C(6)	1.376(6)	S(1)–C(6)	1.706(6)
O(2)–C(9)	1.361(6)	S(1)–C(9)	1.690(7)
O(3)–N(2)	1.394(5)	O(2)–N(2)	1.390(5)
N(2)–C(10)	1.292(6)	N(2)–C(10)	1.278(5)
Bond angles			
O(1)–Sb(1)–O(3)	171.67(12)	O(1)–Sb(1)–O(2)	169.14(13)
C(1)–Sb(1)–C(2)	119.9(2)	C(1)–Sb(1)–C(2)	119.3(2)
C(2)–Sb(1)–C(3)	116.9(2)	C(2)–Sb(1)–C(3)	118.1(2)
C(1)–Sb(1)–C(3)	123.1(2)	C(1)–Sb(1)–C(3)	122.6(3)
O(1)–Sb(1)–C(1)	92.22(17)	O(1)–Sb(1)–C(1)	84.64(18)
O(1)–Sb(1)–C(2)	91.29(18)	O(1)–Sb(1)–C(2)	95.58(18)
O(1)–Sb(1)–C(3)	84.88(17)	O(1)–Sb(1)–C(3)	91.17(19)
O(3)–Sb(1)–C(1)	91.99(17)	O(2)–Sb(1)–C(1)	85.07(18)
O(3)–Sb(1)–C(2)	92.84(18)	O(2)–Sb(1)–C(2)	92.47(17)
O(3)–Sb(1)–C(3)	86.79(17)	O(2)–Sb(1)–C(3)	91.47(18)
Sb(1)–O(1)–N(1)	109.4(3)	Sb(1)–O(1)–N(1)	110.9(2)
O(1)–N(1)–C(4)	111.0(4)	O(1)–N(1)–C(4)	113.1(4)
N(1)–C(4)–C(5)	125.3(5)	N(1)–C(4)–C(5)	126.5(5)
N(1)–C(4)–C(6)	116.1(4)	N(1)–C(4)–C(6)	114.1(5)

3.3. Preparation of [$Pr^i_3Sb(Br)\{ON{=}C(Me)C_5H_4N\text{-}2\}$]

To a stirred benzene solution (15 ml) of [$Pr^i_3Sb\{ON{=}C(Me)C_5H_4N\text{-}2\}_2$] (640 mg, 1.22 mmol), a solution of $Pr^i_3SbBr_2$ in benzene (490 mg, 1.19 mmol) was added and the whole was stirred for 30 min. The solvent was evaporated under vacuum to give nearly quantitative yield (1.099 g, 97%). Similarly all other mono(bromo) complexes were prepared. The trimethylantimony(V) complexes could be isolated as colorless solids and were recrystallized from hexane.

3.4. Preparation of [$Pr^i_3Sb(OH)\{ON{=}C(Me)C_5H_4N\text{-}2\}$]

To a benzene solution (15 ml) of [$Pr^i_3Sb(OH)_2$] (834 mg, 2.93 mmol), a solution of 2-acetylpyridine ketoxime (410 mg, 3.01 mmol) was added with stirring. The whole was refluxed for 4.5 h. The solvent was stripped off in vacuo to give a colorless paste which was recrystallized from hexane (10 ml) at −10EC to yield colorless crystals (770 mg, 65%).

3.5. Controlled hydrolysis of [$Pr^i_3Sb\{ON{=}C(Me)C_5H_4N\text{-}2\}_2$]

To a benzene solution (15 ml) of [$Pr^i_3Sb\{ON{=}C(Me)C_5H_4N\text{-}2\}_2$] (483 mg, 0.93 mmol), methanolic solution (5 ml) of sodium methoxide [prepared from sodium metal (21 mg, 0.91 mmol) in MeOH] was added and refluxed for 2.5 h. After cooling to r.t., 0.2 ml of distilled water was added and stirred for 30 min. The solvents were stripped off under vacuum and residue was extracted with benzene and filtered. The filtrate was concentrated in vacuo and the residue was recrystallized from hexane at −10EC to give colorless crystals of [$Pr^i_3Sb(OH)\{ON{=}C(Me)C_5H_4N\text{-}2\}$].

3.6. Reaction between [$Pr^i_3Sb(OH)_2$] and [$Pr^i_3Sb\{ON{=}C(Me)C_5H_4N\text{-}2\}_2$]

To a $CDCl_3$ solution (0.5 ml) of [$Pr^i_3Sb\{ON{=}C(Me)C_5H_4N\text{-}2\}_2$] (82 mg, 0.157 mmol), solid [$Pr^i_3Sb(OH)_2$] (45 mg, 0.157 mmol) was added in a 5 mm NMR tube. Progress of the reaction was monitored by ^1H-NMR spectroscopy.

Table 4
Selected bond lengths (Å) and bond angles (°) for $2\text{-}OC_4H_3C(Me)$=NOH (**5**) and $2\text{-}SC_4H_3C(Me)$=NOH (**6**) [a]

$2\text{-}SC_4H_3C(Me)$=NOH (**6**)		$2\text{-}OC_4H_3C(Me)$=NOH (**5**)							
Bond lengths									
H(1)–O(1)	0.77(2)	H(1)–O(1)	0.98(6)						
H(1)–N(1)N	2.08(2)	H(1)–N(1)O	1.85(6)						
O(1)–N(1)	1.4071(16)	O(1)–N(1)	1.418(6)	O(3)–N(2)	1.420(7)	O(5)–N(3)	1.405(6)		
O(1)–N(1)N	2.7986(19)	O(1)–N(1)O	2.796(6)	O(3)–N(2)ON	2.793(6)	O(5)–N(3)OO	2.776(7)		
N(1)–C(1)	1.282(2)	N(1)–C(1)	1.316(8)	N(2)–C(7)	1.297(10)	N(3)–C(13)	1.282(10)		
C(1)–C(2)	1.497(2)	C(1)–C(2)	1.502(10)	C(7)–C(8)	1.524(10)	C(13)–C(14)	1.479(10)		
C(1)–C(3)	1.460(2)	C(1)–C(3)	1.470(12)	C(7)–C(9)	1.414(11)	C(13)–C(15)	1.462(10)		
C(3)–C(4)	1.374(2)	C(3)–C(4)	1.341(12)	C(9)–C(10)	1.336(12)	C(15)–C(16)	1.372(11)		
C(4)–C(5)	1.423(2)	C(4)–C(5)	1.436(9)	C(10)–C(11)	1.482(10)	C(16)–C(17)	1.397(10)		
C(5)–C(6)	1.355(2)	C(5)–C(6)	1.347(9)	C(11)–C(12)	1.348(10)	C(17)–C(18)	1.334(11)		
S(1)–C(3)	1.7245(15)	O(2)–C(3)	1.338(9)	O(4)–C(9)	1.343(9)	O(6)–C(15)	1.434(8)		
S(1)–C(6)	1.7094(17)	O(2)–C(6)	1.391(10)	O(4)–C(12)	1.387(9)	O(6)–C(18)	1.358(10)		
Bond angles									
H(1)–O(1)–N(1)	100.9(15)	H(1)–O(1)–N(1)	115(3)						
O(1)–H(1)–N(1)N	156(2)	O(1)–H(1)–N(1)O	159(5)						
O(1)–N(1)–C(1)	112.46(12)	O(1)–N(1)–C(1)	111.1(6)	O(3)–N(2)–C(7)	113.3(6)	O(5)–N(3)–C(13)	108.9(6)		
N(1)–C(1)–C(2)	123.77(14)	N(1)–C(1)–C(2)	122.3(8)	N(2)–C(7)–C(8)	121.0(7)	N(3)–C(13)–C(14)	128.2(7)		
N(1)–C(1)–C(3)	115.71(13)	N(1)–C(1)–C(3)	115.3(7)	N(2)–C(7)–C(9)	117.2(7)	N(3)–C(13)–C(15)	116.8(7)		
C(2)–C(1)–C(3)	120.53(13)	C(2)–C(1)–C(3)	122.0(7)	C(8)–C(7)–C(9)	121.8(7)	C(14)–C(13)–C(15)	115.1(6)		
C(1)–C(3)–C(4)	128.47(13)	C(1)–C(3)–C(4)	129.1(7)	C(7)–C(9)–C(10)	129.8(8)	C(13)–C(15)–C(16)	136.7(7)		
C(3)–C(4)–C(5)	112.54(14)	C(3)–C(4)–C(5)	105.2(7)	C(9)–C(10)–C(11)	105.7(7)	C(15)–C(16)–C(17)	107.0(7)		
C(4)–C(5)–C(6)	112.60(14)	C(4)–C(5)–C(6)	105.8(7)	C(10)–C(11)–C(12)	104.9(7)	C(16)–C(17)–C(18)	108.7(7)		
S(1)–C(3)–C(1)	120.71(11)	O(2)–C(3)–C(1)	117.3(6)	O(4)–C(9)–C(7)	118.2(7)	O(6)–C(15)–C(13)	115.5(7)		
S(1)–C(3)–C(4)	110.81(11)	O(2)–C(3)–C(4)	113.6(7)	O(4)–C(9)–C(10)	111.9(7)	O(6)–C(15)–C(16)	107.7(7)		
S(1)–C(6)–C(5)	112.06(12)	O(2)–C(6)–C(5)	111.1(7)	O(4)–C(12)–C(11)	110.5(7)	O(6)–C(18)–C(17)	110.9(7)		
C(3)–S(1)–C(6)	91.99(8)	C(3)–O(2)–C(6)	104.2(6)	C(9)–O(4)–C(12)	106.8(6)	C(15)–O(6)–C(18)	105.7(6)		

[a] Symmetry equivalent positions $(-x, -y, -z)$ given by a prime, $(-y, x-y, -1/3+z)$ given by a double prime, $(1-y, x-y, -1/3+z)$ given by a triple prime and $(-x+y, 1-x, 1/3+z)$ given by quadruple prime.

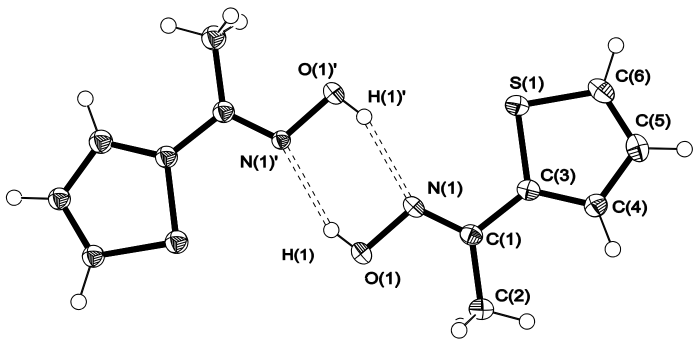


Fig. 4. ORTEP plot showing the hydrogen bonding between pairs of molecules of $2\text{-}SC_4H_3C(Me)$=NOH (**6**). The atoms are drawn with 50% probability ellipsoids.

3.7. X-ray structure determination

Colorless block crystals of [Me_3Sb{ON=C(Me)-C_4H_3O-2}$_2$] (**3**), [Me_3Sb{ON=C(Me)C_4H_3S-2}$_2$] (**4**), $2\text{-}OC_4H_3C(Me)$=NOH (**5**) and $2\text{-}SC_4H_3C(Me)$=NOH (**6**) were mounted on glass fibers. Data were collected in an Enraf–Nonius Kappa CCD area detector (f scans and w scans to fill asymmetric unit) at the University of Southampton EPSRC National Crystallography Service. Data collection and cell refinement [26] gave cell constants corresponding to monoclinic (**3**, **4** and **6**) and trigonal (**5**) cells whose dimensions are given in Table 2 along with other experimental parameters. An absorption correction was applied [27] which resulted in transmission factors ranging from 0.9689 to 0.8573, 0.7299 to 0.6750, 0.9898 to 0.9798 and 0.9184 to 0.85850 for **3**, **4**, **5** and **6**, respectively.

The structures were solved by direct methods [28] and the structures were refined using the WinGX version [29] of SHELX-97 [30]. All of the non-hydrogen atoms were treated anisotropically. In **3** and **4**, all hydrogen atoms were included in idealized positions

Table 5
Physical and analytical data of trialkylantimony(V) complexes

Complexes	Recrystallization solvent (% yield)	M.P. (°C)	% Analysis Found (Calc.)				
			C	H	N	Sb	Br
$[Me_3Sb\{ON{=}C(Me)C_5H_4N\text{-}2\}_2]$	Hexane (83)	71	46.2 (46.7)	5.2 (5.3)	12.8 (12.8)	27.2 (27.8)	
$[Me_3Sb(Br)\{ON{=}C(Me)C_5H_4N\text{-}2\}]$	Hexane (79)	151	32.1 (31.4)	4.0 (4.2)	7.0 (7.3)	31.4 (31.9)	20.6 (20.9)
$[Pr^i_3Sb\{ON{=}C(Me)C_5H_4N\text{-}2\}_2]$	(99)					23.0 (23.3)	
$[Pr^i_3Sb(Br)\{ON{=}C(Me)C_5H_4N\text{-}2\}]$	(99)					25.7 (26.1)	17.6 (17.1)
$[Pr^i_3Sb(OH)_2]$	Dichloromethane (60)	95	37.3 (37.9)	7.6 (8.1)		42.2 (42.7)	
$[Pr^i_3Sb(OH)\{ON{=}C(Me)C_5H_4N\text{-}2\}]$	Hexane (65)	67	47.2 (47.7)	6.8 (7.2)	6.3 (6.9)	29.9 (30.2)	
$[Me_3Sb\{ON{=}C(Me)C_4H_3O\text{-}2\}_2\}$	Hexane (79)	82	43.1 (43.4)	4.8 (5.0)	6.3 (6.7)	29.0 (29.3)	
$[Me_3Sb(Br)\{ON{=}C(Me)C_4H_3O\text{-}2\}]$	Hexane (77)	160	28.7 (29.1)	3.7 (4.0)	3.3 (3.7)	32.4 (32.8)	21.0 (21.5)
$[Pr^i_3Sb\{ON{=}C(Me)C_4H_3O\text{-}2\}_2\}$	(88)	24.8 (24.4)					
$[Pr^i_3Sb(Br)\{ON{=}C(Me)C_4H_3O\text{-}2\}]$	(94)	27.0 (26.7)	17.9 (17.6)				
$[Me_3Sb\{ON{=}C(Me)C_4H_3S\text{-}2\}2]$	Hexane (80)	81	39.9 (40.3)	4.6 (4.7)	6.0 (6.3)	26.9 (27.2)	
$[Me_3Sb(Br)\{ON{=}C(Me)C_4H_3S\text{-}2\}]$	Hexane (80)	169	28.2 (27.9)	3.6 (3.9)	3.2 (3.6)	30.9 (31.4)	20.3 (20.6)

with C–H set at 0.95 Å and with isotropic thermal parameters set at 1.2 times that of the carbon atom to which they were attached. In **5**, the hydrogen atoms attached to carbon were included in idealized positions with C–H set at 0.95 Å and with isotropic thermal parameters set at 1.2 times that of the carbon atom to which they were attached. One of the hydrogen atom attached to oxygen, O(1), was located in the difference map and refined isotropically. The crystal was twinned with the resulting BASF scale factor having the value 0.5123. In **6**, all hydrogen atoms were located in the difference map and refined isotropically. The final cycle of full-matrix least-squares refinement [20] was based on 3989 for **3**, 3739 for **4**, 3350 for **5** and 1500 for **6** observed reflections (2598 for **3**, 2718 for **4**, 2500 for **5** and 1328 for **6** (for $F^2 > 4\sigma F^2$)) and 205 for **3** and **4**, 257 for **5** and 150 for **6** variable parameters and converged (largest parameter shift was 0.001 times its esd). Extinction coefficients for **3**, **4** and **6** were 0.0006(5), 0.0027(7) and 0.009(7), respectively. Bond distances and bond angles are given in Tables 3 and 4 and the molecules are displayed in the ORTEP diagrams in Figs. 1–4.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 166684–166687 for compounds **3**–**6**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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