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CRYSTAL STRUCTURE AND COORDINATION CHEMISTRY OF $Cl_3SnCH_2CH_2CH_2CO_2Et$

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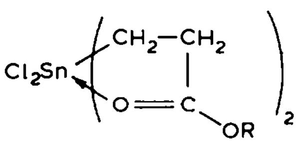
Summary

The crystal and molecular structure of $Cl_3SnCH_2CH_2CH_2CO_2Et$ is reported. Crystals of $Cl_3SnCH_2CH_2CH_2CO_2Et$ are monoclinic, space group $P2_1/c$ with a 8.0242(5), b 11.571(5), c 13.129(12) Å and β 104.54(6)°. The tin atom is 5 coordinate with two chlorines and carbon equatorial and the remaining chlorine and the carbonyl oxygen axial, in a distorted trigonal bipyramidal arrangement: $(Sn–Cl)_{ax}$ 2.382(4) Å, average $(Sn–Cl)_{eq}$ 2.310(3), Sn–C 2.125(12), Sn–O 2.405(8) Å. The six-membered chelate ring is slightly boat-shaped.

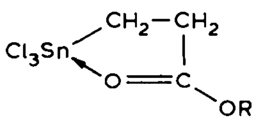
Coordination of the carbonyl group to tin persists in solution but is broken on complexation to $Cl_3SnCH_2CH_2CH_2CO_2Et$ by strong nitrogen donors (2,2′-bipyridyl, 1,10-phenanthroline and pyridine (2 moles)). Comparison of the formation constants for adducts of $Cl_3Sn(CH_2)_nCO_2Et$ (A, $n = 2$ or 3), both chelates with monodentate donors, D, suggests comparable acceptor strengths for A ($n = 2$) and A ($n = 3$) for 1/1 adduct formation but that A ($n = 2$) is a weaker acceptor for 2D/A formation.

Introduction

3-Alkoxy- and 3-aryloxy-3-oxopropyltin chlorides $Cl_2Sn(CH_2CH_2CO_2R)_2$ (I) and $Cl_3SnCH_2CH_2CO_2R$ (II), the so-called estertin chlorides, have attracted consid-

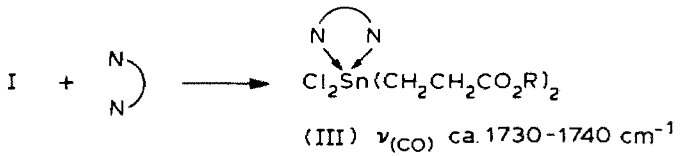


(I) $\nu_{(CO)}$ ca. 1680 cm^{-1} in KBr disc

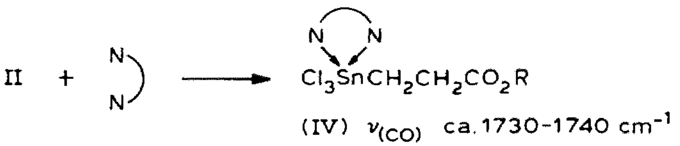


(II) $\nu_{(CO)}$ ca. 1660 cm^{-1} in KBr disc erable attention ever since the discovery of convenient preparative routes by Akzo chemists [1,2]. Compounds I and II have 5-membered chelated structures in both the solid state and in solution [3,4] as shown for example by the crystal structure determination for I (R = Me) and II (R = Me) as well as by IR.

The intramolecular carbonyl coordination in I and II can be broken on coordination by a strong bidentate nitrogen donor, such as 2,2′-bipyridyl(bipy) or 1,10-phenanthroline (phen) [4]:

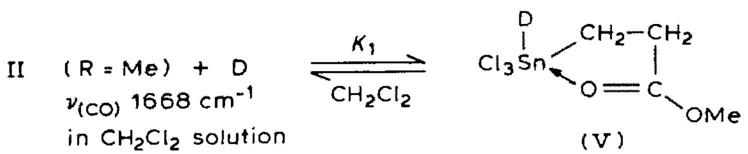


(1)



(2)

The 1/1 complexes, III and IV, are essentially undissociated in CH_2Cl_2 solution [4]. 1/1 complexes V are also formed between II and monodentate nitrogen donors, D, e.g. D = pyridine (py), quinoline or aniline, in CH_2Cl_2 solution; in complexes V, the carbonyl coordination is still intact, as shown by ν(CO) ca. 1650 cm^{-1}. Coordination of a second molecule of pyridine (but not the weaker donors) provides a 2/1 complex in which the carbonyl–tin coordination is broken [4].



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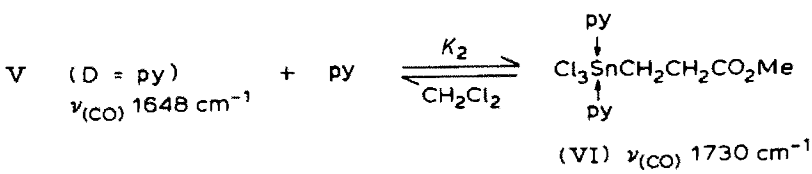


(4)

A related compound to II, viz. $Cl_3SnCH_2CH_2CH_2CO_2Et$ (VII) has been prepared and in this paper we report both on its crystal structure and its behaviour as a Lewis acid.

Experimental

4-Ethoxy-4-oxobutyl bromide, $BrCH_2CH_2CH_2CO_2Et$, ν(CO) 1745 cm^{-1} was obtained from γ-butyrolactone and HBr in ethanol [5].

(4-Ethoxy-4-oxobutyl)triphenyltin, $Ph_3SnCH_2CH_2CH_2CO_2Et$

Sodium wire (6.25 g) and naphthalene (6.95 g, 0.054 *M*) in dimethoxyethane

(DME) (250 ml) was stirred under nitrogen for 1.5 h at ambient temperature. A solution of triphenyltin chloride (52.4 g, 0.135 mol) in DME (200 ml) was added at such a rate to maintain the green colour of sodium naphthalene (ca. 4 h) [6]. The reaction mixture was cooled to $-60°C$ and 4-ethoxy-4-oxobutyl bromide (104 g, 0.540 mol) was slowly added with stirring. Stirring was continued, after the addition was complete, for 2 h at $-60°C$ and then the reaction mixture was allowed to reach ambient temperature and was left overnight.

A saturated aqueous solution of ammonium chloride (50 ml) was added and the organic layer collected. The aqueous layer was extracted with DME (2×25 ml portions). The combined organic layers were dried (magnesium sulphate) and the solvent removed to leave an oil, which solidified on cooling, m.p. ca. 20°C. Yield 83%, ν(CO) 1735 cm^{-1}. Analysis. Found: C, 61.6; H, 5.5; Sn 24.9. $C_{24}H_{26}O_2Sn$ calcd.: C, 61.9, H, 5.6, Sn, 25.6%. ^1H NMR (220 MHz, $CDCl_3$): δ 7.52 (d, 6H, *ortho* H of phenyl groups, J ($^{117,119}Sn$–H) 27 Hz), 7.34 (m, 9H, *meta* and *para* of phenyl groups, 4.07 (quart. 2H, OCH_2CH_3, J(H–H) 8 Hz), 2.35 (t, 2H, $SnCH_2CH_2CH_2$, J 7 Hz), 2.01 (quintet, 2H, $SnCh_2CH_2CH_2$), 1.49 (t, 2H, $SnCH_2CH_2CH_2$, J(H–H) 7Hz, J (^{117},^{119}Sn–^1H) 30 Hz), 1.24 (t, 3H, OCH_2CH_3, 7 Hz).

Trichloro(4-ethoxy-4-oxobutyl)tin, $Cl_3SnCH_2CH_2CH_2CO_2Et$

Tin(IV) tetrachloride (53.6 g, 0.205 mol) was slowly added to Ph_3SnCH_2-$CH_2CH_2CO_2Et$ (31.8 g, 0.068 mol) and the mixture was heated at 110°C for 2 h. After cooling, the mixture was extracted with hot carbon tetrachloride. Addition of hexane to the CCl_4 extract results in the precipitation of $Cl_3SnCH_2CH_2CH_2CO_2Et$. This was recrystallized from CH_2Cl_2/hexane; m.p. 96°C, yield 16.8 g, 72%, ν(CO) Nujol mull 1645 cm^{-1}. Analysis. Found: C, 21.3; H, 3.1; Cl, 31.3; Sn, 34.2. $C_6H_{11}Cl_3O_2Sn$ calcd.: C, 21.1; H, 3.2; Cl, 31.2; Sn, 34.9%. ^1H NMR (220 MHz, $CDCl_3$) δ 4.32 (quart. 2H, OCH_2CH_3, J(H–H) 7Hz), 2.61 (br, 2H, $SnCH_2CH_2CH_2$), 2.30 (br, 4H, $SnCH_2CH_2CH_2$, J($^{117,119}Sn$–^1H, 42 Hz), 1.35 (t, 3H, OCH_2CH_3, J(H–H) 7 Hz). Mössbauer data: IS 1.16 ± 0.01 mm sec^{-1}, QS 2.09 ± 0.01 mm sec^{-1}.

Trichloro(3-ethoxy-3-oxopropyl)tin, $Cl_3SnCH_2CH_2CO_2Et$, was prepared by the reaction of $SnCl_2$, HCl and $CH_2{=}CHCO_2Et$ as previously reported [1,2].

Solvents were dried over calcium hydride and distilled before use. The donors used in this study were recrystallized or redistilled commercial samples.

Determination of equilibrium constants

Equilibrium constants for interactions of $Cl_3Sn(CH_2)_nCO_2Et$ ($n = 2$ or 3) and donors in CH_2Cl_2 solution were obtained, as previously described [4], using UV or IR data. Solutions were made up and optical cells filled within a dry box. Absorptions were measured at suitable wavelengths for a number of solutions containing different concentrations of a particular donor–acceptor pair. Concentrations were so chosen to give as great a spread of complexation as possible.

Determination of the crystal structure of $Cl_3SnCH_2CH_2CH_2CO_2Et$

Crystal data. Trichloro(4-ethoxy-4-oxobutyl)tin is monoclinic (oscillation photographs about all three axes) with a 8.042(5), b 11.571(5), c 13.129(12) Å and β 104.54(6)°. The space group is $P2_1/c$ (from systematic absences $0k0$ present for $k = 2n$ and $h0l$ present for $l = 2n$). The cell contains 4 molecules giving an X-ray density of 1.910 g/cm^3 for the molecular weight of 340.2.

TABLE 1

FINAL ATOMIC PARAMETERS OF $Cl_3Sn(CH_2)_3CO_2Et$

(Estimated standard deviations applicable to the least significant figures are given in parentheses. Fractional coordinates are $\times 10^4$ and B_{iso} are $\times 10$.)

	x/a	y/b	z/c	
Sn	−108(1)	2048(1)	567(1)	43 [a]
Cl(1)	885(5)	905(3)	2027(2)	53 [a]
Cl(2)	−1490(6)	3632(3)	1061(4)	78 [a]
Cl(3)	−2662(4)	962(3)	−109(3)	62 [a]
O(1)	2355(10)	3197(7)	1391(6)	52(2)
O(2)	4058(11)	4658(8)	1357(7)	60(2)
C(1)	962(15)	2092(11)	−756(9)	51(2)
C(2)	2864(16)	2245(11)	−538(9)	51(2)
C(3)	3496(16)	3462(11)	−125(10)	53(3)
C(4)	3261(14)	3736(10)	933(9)	44(2)
C(5)	3766(20)	5079(14)	2367(12)	71(3)
C(6)	4094(23)	6365(17)	2431(14)	85(4)

[a] Calculated from anisotropic thermal parameters so that $B_{iso} = 4/3\ (a^2B_{11} + b^2B_{22} + c^2B_{33} + ac \cos \beta\ B_{13})$ which give an anisotropic vibration correction of the form $\exp -(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{23}kl + B_{12}hk + B_{13}hl)$.

The unit cell and intensity data were obtained on a Nicolet P5 four circle diffractometer using monochromated Mo radiation. The crystal used had dimensions $0.375 \times 0.375 \times 0.05$ mm. The $2\theta/\theta$ scan data collection procedure, with 2ϑ in the range 0–50° yielded 1803 unique intensities ($I > \sigma/2$). No absorption correction was applied.

The crystallographic calculations were performed on the Honeywell 66/80 computer, of the Computing Centre of the University of Aberdeen, using MULTAN 78

TABLE 2

BOND LENGTHS (Å) AND ANGLES (deg) OF $Cl_3SnCH_2CH_2CH_2CO_2Et$

(Values in parentheses are estimated standard deviations associated with the least significant digits.)

Bond lengths			
Sn–Cl(1)	2.301(3)	C(1)–C(2)	1.495(18)
Sn–Cl(2)	2.319(4)	C(2)–C(3)	1.548(18)
Sn–Cl(3)	2.382(4)	C(3)–C(4)	1.482(17)
Sn–O(1)	2.405(8)	C(4)–O(1)	1.225(14)
Sn–C(1)	2.125(12)	C(4)–O(2)	1.297(15)
O(2)–C(5)	1.486(17)	C(5)–C(6)	1.510(25)
Angles			
Cl(1)–Sn–Cl(2)	108.2(1)	Sn–C(1)–C(2)	116.8(8)
Cl(1)–Sn–Cl(3)	95.4(1)	C(1)–C(2)–C(3)	113.9(10)
Cl(2)–Sn–Cl(3)	95.3(1)	C(2)–C(3)–C(4)	114.6(10)
Cl(1)–Sn–O(1)	82.5(2)	C(3)–C(4)–O(1)	125.7(10)
Cl(1)–Sn–C(1)	124.6(3)	C(3)–C(4)–O(2)	114.4(10)
Cl(2)–Sn–O(1)	80.5(2)	O(1)–C(4)–O(2)	119.9(10)
Cl(2)–Sn–C(1)	122.1(4)	Sn–O(1)–C(4)	125.7(7)
Cl(3)–Sn–O(1)	174.4(2)	C(4)–O(2)–C(5)	118.7(10)
Cl(3)–Sn–C(1)	101.3(3)	O(2)–C(5)–C(6)	107.9(13)
O(1)–Sn–C(1)	84.2(4)		

[7] and the NRC crystallographic package [8], and scattering factors for neutral atoms taken from the International Tables for X-Ray Crystallography [9].

The position of the Sn and one Cl atom were obtained from MULTAN 78 and

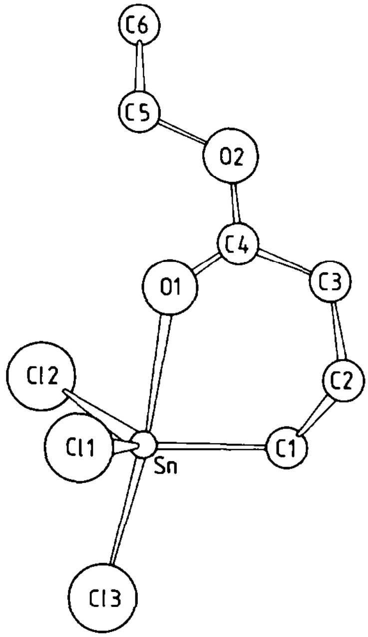


Fig. 1. The molecular structure and atomic labelling in $Cl_3SnCH_2CH_2CH_2CO_2Et$.

two successive cycles of structure factor calculations, followed by preparation of an electron density map, revealed first the remaining two Cl atoms and then all of the remaining non-hydrogen atoms. The structure was refined by block diagonal least

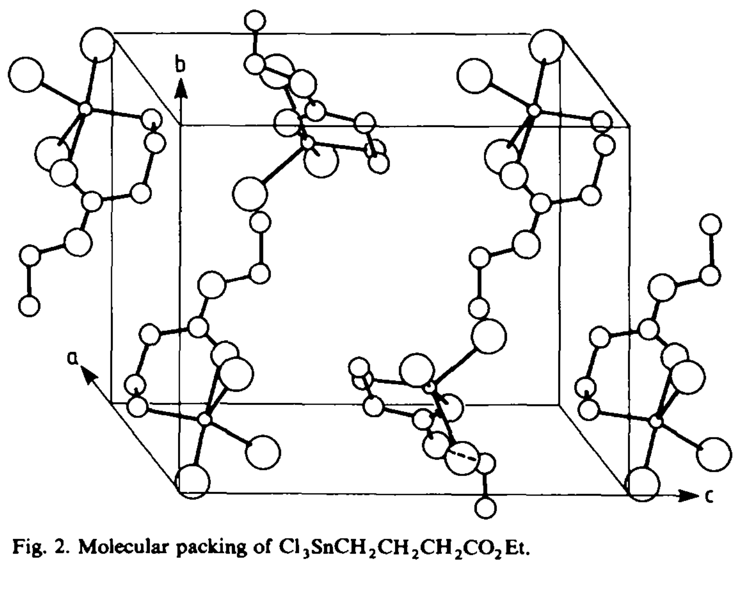


Fig. 2. Molecular packing of $Cl_3SnCH_2CH_2CH_2CO_2Et$.

squares where the observations were weighted according to $w = 1/\{1 + [(|F_o| - P2)/P1]^2\}$ where $P1 = 30$ and $P2 = 50$, and Sn and Cl atoms were vibrating anisotropically to a final R value of 7.31%. At this stage, shifts in parameters were less than 1/100 of the corresponding estimated standard deviations, the distributions of $\Sigma w\Delta^2$ against sin θ and against $|F_o|$ were satisfactory, and the difference map was essentially featureless.

The final atomic parameters are given in Table 1, selected bond lengths and angles are in Table 2; Tables of observed and calculated structure factors and of anisotropic thermal vibration parameters are available from the authors.

Figure 1 shows the shape of the molecule and the atom numbering scheme; the packing diagram is illustrated in Fig. 2.

Results and Discussion

Structure of $Cl_3SnCH_2CH_2CH_2CO_2Et$ (VII). Compound VII exists in the solid state as a six-membered chelate, in which the carbonyl oxygen is coordinated to tin, as in the five-membered chelate II (R = Me) [3]. The structure of VII consists of discrete molecules with no intermolecular contacts less than 3.58 Å. The tin atom is 5-coordinate with Cl(1), Cl(2) and C(1) equatorial and with Cl(3) and O(1) (the carbonyl oxygen) axial atoms in a distorted trigonal bipyramidal arrangement (Fig. 1). There is therefore considerable similarity between the structures of II and VII.

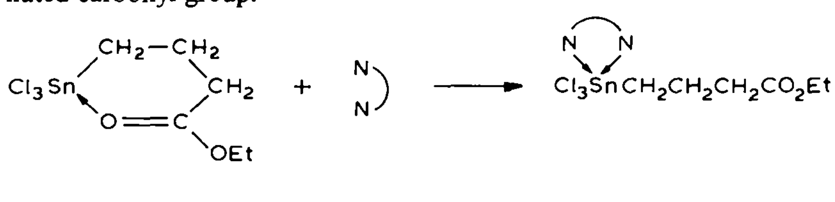
The six-membered chelated ring in VII, comprised of atoms Sn, C(1)–C(4) and O(1), is slightly boat-shaped with C(2) and O(1), 0.7 and 0.24 Å, respectively, out of the plane of the remaining atoms of the ring.

As expected the axial Sn–Cl bond length, 2.382(4) Å, is longer than the equatorial ones, 2.301(3) and 2.319(4) Å; a similar result, for example, was found for II (R = Me) with $(Sn–Cl)_{eq}$ 2.303(2) and 2.317(2) and $(Sn–Cl)_{ax}$ 2.357(2) Å [3]. The Sn–C bond length, 2.125(12) Å is unexceptional, e.g. Sn–C in II (R = Me) is 2.139(8) Å [3]. The coordinate Sn–O bond distance in VII is 2.405(8) Å, which is only slightly longer than those in Me_3SnCl: $Ph_3PCHCOMe$ (2.332(6) Å) [10] and in $Ph_3SnONPhCOPh$ (2.308(4) Å) [11]. Comparison with the Sn–O bond length found for II (R = Me) (2.347(5) Å) [3] reveals a longer coordinate bond in VII (2.405(8) Å). This indicates a weaker coordination in the six-membered chelate VII than in the five-membered chelate II (R = Me) in the solid state. As the formation constants for adducts of II and VII show, there is evidence for this in solution, too.

The ν(CO) value of VII (1663 cm^{-1}) in CH_2Cl_2 solution indicates that the carbonyl coordination persists in this phase too.

Reactions with external donors. Interactions of VII with various nitrogen donors were studied in CH_2Cl_2 solution in a similar manner to that followed previously for estertin chlorides, including II (R = Me) [4].

Bidentate donors, such as bipy and phen, and VII formed 1/1 complexes, which were essentially undissociated in CH_2Cl_2 solution at 25°C, as shown by UV and IR spectra; ν(CO) of the 1/1 complexes (ca. 1740 cm^{-1}) clearly points to an uncoordinated carbonyl group.



(5)

TABLE 3

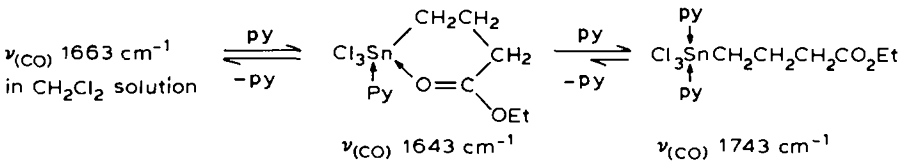
STABILITY CONSTANTS [a] FOR ADDUCTS OF $Cl_3Sn(CH_2)_nCO_2R$ AND DONORS, D, IN CH_2Cl_2 SOLUTION AT 25 ± 0.1°C

Donor	$Cl_3SnCH_2CH_2CH_2CO_2Et$ [b]		$Cl_3SnCH_2CH_2CO_2Et$ [b]		$Cl_3SnCH_2CH_2CO_2Me$ [c]	
	log K_1	log K_2	log K_1	log K_2	log K_1	log K_2
Pyridine [d]	> 5	1.97 ± 0.1	> 5	0.89 ± 0.06	> 5	0.80 ± 0.1
Aniline [e]	1.48 ± 0.10	-	1.52 ± 0.10	-	1.50 ± 0.10	-
Quinoline [f]	2.37 ± 0.10	-	2.45 ± 0.10	-	2.27 ± 0.10	-

[a] $K_1 = [Cl_3Sn(CH_2)_nCO_2R.D]/[D][Cl_3Sn(CH_2)_nCO_2R]$; $K_2 = [Cl_3Sn(CH_2)_nCO_2R.2D]/[D][Cl_3Sn(CH_2)_nCO_2R \cdot D]$. [b] This study. [c] Ref. 3. [d] Stability constants calculated from IR absorptions in the carbonyl region. [e] Stability constants calculated from absorptions at λ_{max} (288 nm) of aniline. [f] Stability constants calculated from the absorptions at λ_{max} (273 nm) of quinoline and absorptions (310–330 nm) of complex.

Monodentate donors (pyridine, aniline and quinoline) in CH_2Cl_2 solution all formed 1/1 complexes, in which the carbonyl group was still coordinated to tin (ν(CO) ca. 1640–1645), and so the 1/1 complexes contain 6 coordinate tin. Unfortunately it was not possible to isolate these complexes as pure solids. The aniline and quinoline complexes were extensively dissociated in solution (see Table 3 for formation constants). In contrast, pyridine, the strongest of the 3 donors studied, formed a 1/1 complex which was largely undissociated at ambient temperature (the formation constant was > 10^5 and too high to measure). Furthermore it was possible to form a 2/1 complex with pyridine and to obtain its formation constant from the 1/1 adduct. As also found with the analogous 1/1 complexes of II [4], the

VII



coordination of the first monodentate donor to these carboxyalkyltin trichlorides results in a shift in ν(CO) of ca. 20 cm^{-1} to lower values.

Comparison of formation constants for adducts of II (R = Et) and VII. Formation constants were also determined for adducts of II (R = Et) in order to allow a comparison to be made of the acceptor strengths of II (R = Et) and VII. Previously we had determined some values for adducts of II (R = Me); however it was thought prudent to compare acceptor strengths of compounds having the same ester grouping in case different groups unduly influenced matters. (As shown in Table 3, there is however scarcely any difference between the acceptor strengths of II (R = Me) and II (R = Et)).

From the values of the formation constants, assembled in Table 3, it appears that the first monodentate donor molecule associates equally well to II (R = Et) and to VII to give 1/1 complexes, in which the carbonyl–tin coordination has not been broken.

However a difference was detected with the 2/1 pyridine complexes. As the values of the formation constant indicate, it is easier to form 2/1 complexes (in which the Sn–O coordination is broken) with VII than with II (R = Et) by a factor of 12. This suggests that the internal coordination in VII is easier to break than that in II (R = Et), i.e. the 6-membered chelate in VII is weaker than the 5-membered chelate in II (R = Et).

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