An Unusual Configuration for a Bis(4-acylpyrazolon-5-ate)diorganotin Species

Francesco Caruso,[*,†] Miriam Rossi,[‡] Fabio Marchetti,[§] and Claudio Pettinari[*,§]

Istituto di Strutturistica Chimica "G. Giacomello", CNR, CP 10, 00016 Monterotondo Stazione, Roma, Italy, Department of Chemistry, Vassar College, Poughkeepsie, New York 12604-0484, and Dipartimento di Scienze Chimiche, Università degli Studi, via S. Agostino 1, 62032 Camerino, Macerata, Italy

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Summary: The molecular structure of bis[1-(4-(trifluoromethyl)phenyl)-3-methyl-4-benzoylpyrazolon-5-ato]dimethyltin(IV) determined by X-ray diffraction methods shows an octahedral configuration with the metal on an inversion center. In this anomalous anti configuration equal Sn−O and C−O bond lengths in each ligand indicate a symmetrical O,O′ bidentate form. In addition to this octahedral species, ^{119}Sn NMR in $CDCl_3$ shows a 5-coordinate complex, probably due to the loss of a Sn−O(acyl) bond.

4-Acyl-5-pyrazolones (Figure 1) are widely used as metal extractants because of their good donor ability and low cost.[1] Since their alkali-metal salts possess good solubility in water, acid aqueous solutions of some metals can be treated with them. Upon addition of an organic solvent, the metal 4-acyl-5-pyrazolonate species is recovered from extraction in the organic phase; alternatively, recovery of the metal is obtained by precipitation. Further, some 4-acyl-5-pyrazolonates are used as dyes.[2]

Potential substitution on these ligands are at the R^1, R^2, and R^3 positions. Until recently the only R^1 substituent was Ph. Then the first ligands (and some metal complexes) containing R^1 = methyl[3a] were reported by us; R^2 is exclusively a methyl group while, in contrast, R^3 is easily varied. Data show that the extraction properties of these ligands can be tuned through the right choice of R^1, R^2, and R^3. Thus, methyl substituents on the ligand induce better complex affinity for aqueous solution, whereas phenyl substituents induce solubility in the organic phase.[4]

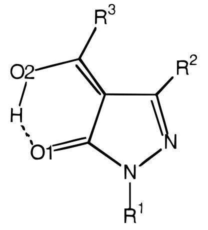

Figure 1. 4-Acyl-5-pyrazolone proligands (LH).

Crystal structures of rare-earth-metal (U, Eu, Tb),[5] transition-metal (Cu, Fe),[6] and main-group-metal (Sn, Hg, Tl, Pb, Ca, Sb)[3] derivatives of these ligands have been reported.

The chelating 4-acyl-5-pyrazolonates show the metal−O1(pyrazolone) bond to be exclusively covalent. In addition, the metal−O2(acyl) bond can be covalent but for organotin compounds the Sn−O2 bond length is generally much longer than Sn−O1.[3a] The ligand can contribute to supramolecular architecture in its trialkyltin derivatives, where the metal links only one O atom and the other carbonyl is involved in a H bond with a nitrogen from another molecule;[7] in contrast, triaryltin derivatives are chelates. Furthermore, an O2,N-exo-tridentate form was also observed in a Pb(II) derivative.[3c]

For diorganotin derivatives, L_2SnR_2, the *syn* structure was dominant, in which the metal polyhedron shows the two 4-acyl-5-pyrazolonate ligands facing each other such that their equivalent arms are closer (Figure 2).[3a] The two R groups complete this 6-coordinate metal configuration, known as skewed trapezoidal bipyramidal (STB).[8] The octahedral geometry is strongly distorted, and the organometallic bond angle C−Sn−C can be as

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[*] To whom correspondence should be addressed. E-mail: F.C., CAR@isc.mlib.cnr.it; C.P., Pettinar@camserv.unicam.it.

[†] CNR.

[‡] Vassar College.

[§] Università degli Studi.

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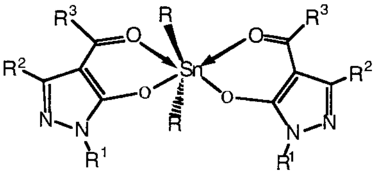

Figure 2.

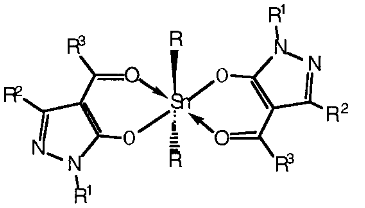

Figure 3.

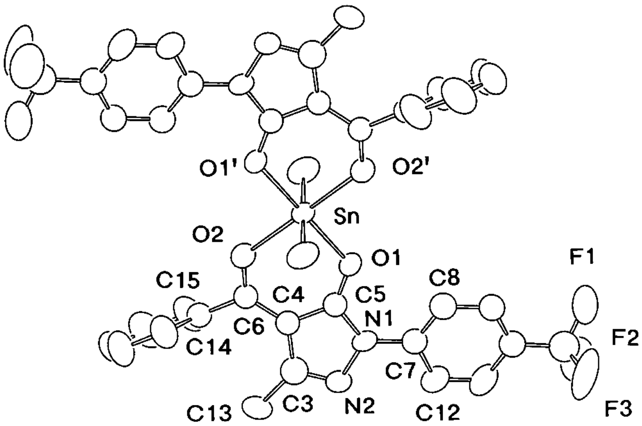

Figure 4. Ortep drawing of the title compound.

small as 150°; the R groups are folded toward the region of the weak Sn−O2 bonds. The C−Sn−C angle is smaller for R = alkyl than for R = Ph.[9]

During the time that we have been studying this system, we always wondered why the centrosymmetrical configuration (Figure 3) had not been observed.

Another reason for our interest in diorganotin compounds is because of their systematic antitumor activity. The National Cancer Institute has screened over 2000 tin derivatives,[10] more than for any other metal. Diorganotins are especially active in P388 leukemia cell lines.

In this note we show that the molecular structure of a diorganotin derivative with the metal bound to a novel 4-acyl-5-pyrazolonate ligand, bis[1-(4-(trifluoromethyl)-phenyl)-3-methyl-4-benzoylpyrazolon-5-ato)]dimethyltin-(IV) ($R^1 = p$-CF_3-Ph, R^2 = methyl, and R^3 = Ph), is an *anti* species (Figure 4), contrary to expectations, and shows the metal on a crystallographic inversion center.

We describe the principal structural features. In contrast with previously related *syn* compounds, the bond distances Sn−O1 (2.214(5) Å) and Sn−O2 (2.220(6) Å) are equal. This symmetric O,O′-bidentate ligand coordination implies equivalent carbonyl bonds as well (C5−O1 = 1.267(9) Å, C6−O2 = 1.273(9) Å). Examples of equal metal−O1 and metal−O2 bond lengths are found in transition-metal 4-acyl-5-pyrazolonates (Cu and Fe).[6] The phenyl ring (R^1) is almost coplanar with the pyrazole ring, and the corresponding dihedral angle is 13.7°. This feature suggests extended resonance through both rings and was also observed in the *syn* configuration of other related organotin derivatives.[3a] The bite angle, O1−Sn−O2 = 85.9(2)°, is the widest ever observed in organotin 4-acyl-5-pyrazolonates.

In the IR spectrum of this complex, the Sn−O stretching bands are of the same order as those found in their equivalent *syn* species.[3a,11] Also, the Sn−C band at 592 cm^{-1} is similar to that of *syn* derivatives.[3a,11] Therefore, IR apparently cannot discriminate between *syn* and *anti* species, although it can distinguish between *cis*-octahedral (Cl_2SnO_2) and distorted *trans*-octahedral (R_2SnO_2) derivatives.[3a,11]

The ^{119}Sn NMR spectrum in benzene-d_6 at room temperature shows only one peak, which can indicate a unique species or a fast-exchanging equilibrium on the NMR time scale. The spectrum does not change after increasing the temperature. The spectrum in $CDCl_3$, performed at room temperature, shows two peaks: one indicates an octahedral configuration, and the other is associated with a trigonal-bipyramidal species, probably due to loss of a Sn−O2 bond, as previously shown by another related species containing $R^3 = CCl_3$.[11] We have also performed the ^{119}Sn NMR analysis in $CDCl_3$ for an equivalent compound containing $R^3 = CF_3$ and found enhanced dissociation, as only the 5-coordinate species is present. For the latter compound ^{19}F NMR spectra confirm the 5-coordinate species. The previously studied derivative containing $R^3 = CCl_3$ reacts further and undergoes a haloformic reaction in alcohol (R′OH), and the R^3 group is changed to OR′.[11] We conclude that electron-withdrawing groups in R^3 induce chemical instability in bis(4-acyl-5-pyrazolonate)diorganotin species, and this is probably due to the tin acidity competitive effect.

The synthesis of the title compound does not differ from that of previously related species[3a,11] (Scheme 1). However, the crystals analyzed by diffraction in this study were obtained directly from the methanol reaction mixture, whereas in previous cases they were obtained after recrystallization from other organic solvents.[3a,11] Therefore the different *anti* stereochemistry of the title compound may arise from this factor.

Scheme 1

$$2HL + 2KOH + Cl_2SnR_2 \rightarrow L_2SnR_2 + 2KCl + 2H_2O$$

One example of different stereochemistry induced by peripheral ligand changes is Ph_2SnCl_2(2,2′-bipyridine) which is a *trans*-diphenyl *cis*-dichloro species, whereas the related (p-tolyl)$_2SnCl_2$(2,2′-bipyridine) compound is a *cis*-ditolyl *trans*-dichloro isomer.[12] Bis(di-R-dithiophosphinate)dimethyltin species behave similarly. Thus, a polymer species is found for R = Ph, whereas a

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monomer is obtained for R = ethyl.[13] Also in bis(dithiocarbamate)lead(II) compounds peripheral N-substitutents change the metal coordination sphere and even the coordination number.[14] In all these examples the changed groups do not interact with other metal units and their role in the formation of variety of molecular species is an open question.

In conclusion, a change in a peripheral area (a CF_3 group instead of H) in the Ph *para* position (R^1) induces a dramatic change in the tin complex: the *syn* species[15] becomes an *anti* species. However, the only difference in the ligand geometry between the *syn* and the *anti* configurations is the electron delocalization in the chelate: it is maximum for the latter and is shown by the equal Sn−O and equal C−O bonds. It is also seen that the intrinsic asymmetry of 4-acyl-5-pyrazolonates does not necessarily imply an STB configuration for their diorganotin derivatives, as was suggested so far.

Experimental Section

Synthesis of Bis[1-(4-(trifluoromethyl)phenyl)-3-methyl-4-benzoylpyrazolon-5-ato]dimethyltin(IV). To a methanol solution (30 mL) of LH (2 mmol) were added KOH (2 mmol) and $(CH_3)_2SnCl_2$ (1 mmol). A yellow precipitate formed immediately. The mixture was stirred overnight, and the precipitate was then filtered off, washed with methanol (ca. 10 mL), and dried under reduced pressure at room temperature. From the filtrate methanol solution good quality crystals slowly appeared. Yield: 82%. Mp: 190−192 °C. Anal. Calcd for $C_{38}H_{30}F_6N_4O_4Sn$: C, 54.38; H, 3.60; N, 6.67. Found: C, 54.12; H, 3.76; N, 6.50. Spectroscopic data are as follows. IR (Nujol, cm^{-1}): 1618 vs, ν(C=O); 592 m, ν(Sn−C); 443 vs, 407 s, ν(Sn−O). ^{1}H NMR [300 MHz, referenced to TMS, in $CDCl_3$; δ): 1.05 s ($^2J(^{119/117}$Sn−^{1}H) = 101.8, 97.5 Hz), 1.20 s ($^2J(^{119/117}$Sn−^{1}H) = 80.8, 76.2 Hz, 6H, Sn−CH_3); 1.88 s, 1.97 s, 2.14 s, (6H, C3−CH_3); 7.50−7.70 m, 8.10 m, 8.20 d (18H, C_6H_5C=O, *p*-CF_3-C_6H_4-N). ^{19}F NMR (282.2 MHz, referenced to $CFCl_3$, in $CDCl_3$, 293 K; δ): −62.9 s. ^{19}F NMR (in $CDCl_3$, 218 K; δ): −62.1 s, −62.2 s, −62.3 s, −62.6 s. ^{119}Sn NMR (111.9 MHz, referenced to $(CH_3)_4Sn$, in $CDCl_3$; δ): −102.0 s, −321.4 s. ^{119}Sn NMR (in benzene-d_6; δ): −324.1s .

Table 1. Summary of Crystal Data

chem formula	$C_{38}H_{30}N_4O_4F_6Sn$
mol wt	839.36
cryst habit	prism
cryst size/mm	0.40 × 0.25 × 0.15
cryst syst	monoclinic
space group	$P2_1/n$ (No. 14)
cryst color	pale yellow
a/Å	9.782(2)
b/Å	9.864(2)
c/Å	19.099(3)
β/deg	100.75(1)
V/Å^3	1809(1)
Z	2
T/K	298
D_{calcd}/Mg m^{-3}	1.541
$2\theta_{max}$/deg	56
μ/cm^{-1}	7.95
wavelength/Å (graphite monochr)	Mo Kα, 0.710 69
scan speed/deg min^{-1}	2
transmissn factors	0.991−1.035
scan range/deg	1.1
no. of measd rflns	4889
no. of unique rflns	4374
no. of refined rflns ($F > 3\sigma(F)$)	1881
no. of refined params	201
R, R_w[a]	0.045, 0.059
S[b]	1.001

[a] $R(F) = \sum|(F_o - F_c)|/\sum F_o$. [b] $S = [\sum\{w(F_o^2 - F_c^2)^2\}/(n - p)]^{0.5}$; n = number of data, and p = number of refined parameters.

Crystal Structure Determination. Crystal data were collected with a Syntex $P2_1$ diffractometer. The structure was solved with Patterson-Fourier methods using CAOS.[16] A ψ-scan was applied. Reflections collected: h, k, $\pm l$. H atoms were considered to ride on their attached C atoms at 0.96 Å, and hydrogen B(iso) values were fixed. A summary of the crystal data is given in Table 1.

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Supporting Information Available: Tables of all geometrical parameters, displacement parameters, and fractional coordinates. This material is available free of charge via the Internet at http://pubs.acs.org.

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