

Short Communication

The structure of *trans*-bis(ethane-1,2-dithiolato[2-]-*S,S'*)bis(3-aminopyrazole)tin(IV)

G. Bandoli and A. Dolmella

Dipartimento di Scienze Farmaceutiche, Università di Padova, via F. Marzolo 5, 35131 Padua (Italy)

V. Peruzzo* and G. Plazzogna

Dipartimento di Chimica Inorganica, Metallorganica ed Analitica, Università di Padova, via F. Marzolo 1, 35131 Padua (Italy)

(Received January 21, 1993; revised March 26, 1993)

Abstract

The 1:2 adduct of bis(ethane-1,2-dithiolato)tin(IV) with 3-aminopyrazole, $[\text{Sn}(\text{C}_2\text{H}_4\text{S}_2)_2(\text{C}_3\text{H}_5\text{N}_3)_2]$, crystallizes in the monoclinic $C2/c$ space group, with $Z=4$, $a=13.122(2)$, $b=11.216(2)$, $c=11.810(2)$ Å and $\beta=98.47(2)^\circ$. The structure determination, based on 2127 independent reflections, has been refined to $R=2.42\%$. The molecules are discrete, monomeric, *trans*-octahedral units, with the tin atom at the centre of symmetry, planar aminopyrazole groups and SnS_2C_2 groups in twist-envelope form. The aminopyrazole ligands act as monodentate and are bonded through the N(2) atoms. No significant intermolecular contacts and $\text{S}\cdots\text{H}-\text{N}$ hydrogen bonds are observed.

Introduction

The biological interest of pyrazolic bases [1] has stimulated many structural studies about the interaction of tin and organotin chlorides with such ligands, and the important role of inter- and intra-molecular hydrogen bonding in such structures has been evidenced [2]. Substrates with lower acceptor ability than halides have not yet been considered. We have recently reported the structure of the adducts of bis(ethane-1,2-dithiolato[2-]-*S,S'*)tin(IV), $[\text{Sn}(\text{edt})_2]$, with pyridine and 2-(2-pyridyl)-ethylamine [3], and we report here the preparation and structure of the adduct of $\text{Sn}(\text{edt})_2$ with the pyrazolic ligand 3-aminopyrazole (apz). X-ray structures of metal complexes with this ligand have not previously been described.

*Author to whom correspondence should be addressed.

Experimental

Trans-bis(ethane-1,2-dithiolato[2-]-*S,S'*)bis(3-aminopyrazole)

$\text{Sn}(\text{edt})_2$ (0.24 g, 0.8 mmol), obtained as in ref. 3, and apz (0.14 g, 0.17 mmol), purchased from Fluka, were dissolved in dichloromethane, and the solutions mixed under agitation. The solvent was left to slowly evaporate at room temperature. After three days, the solution being reduced to a small volume, the colorless crystals formed were filtered, washed with the same solvent and dried (3.6 g, yield 95%). m.p. 141 °C. *Anal.* Calc. for $\text{C}_{10}\text{H}_{18}\text{N}_6\text{S}_4\text{Sn}$: C, 25.60; H, 3.86; N, 17.91; Found: C, 25.7; H, 3.8; N, 18.0%. The IR and far-IR spectra were recorded on a Nicolet 5SXC and a FAR 20F instrument, respectively.

Crystallography

Details of crystal data, measurement of intensity, data processing and refinement procedure are given in Table 1. An empirical absorption correction, based on measurements of six reflections at χ c. 90° for different azimuthal angles (ψ -scans), was made. The structure was solved by standard heavy-atom methods and, in the refinement procedure, hydrogen atoms were fixed at their geometrical positions, with a common, variable isotropic thermal factor. The largest peak ($1.2 \text{ e } \text{Å}^{-3}$) on the final difference map was close to the Sn atom (0.75 Å). Fractional atomic coordinates and equivalent thermal parameters are given in Table 2, while bond distances and angles are listed in Table 3. For additional data, see 'Supplementary material'.

Results and discussion

The Lewis acidity of $\text{Sn}(\text{edt})_2$ is much lower than that of SnCl_4 and the formation of addition compounds requires ligands with appreciable basicity and low hindrance [4]. In fact the $\text{p}K_a$ of $[\text{apzH}]^+$ is about 5.5, close to that of pyridine (5.2) [5], which gives 1:1 and 1:2 adducts [3, 4]. Theoretical calculations have shown that in apz the amino form is stable with respect to the tautomeric iminic one [6]. Moreover ^{13}C NMR studies indicate that protonation takes place on the pyrazolic nitrogen atom, while double protonation was not observed [7]. Accordingly, the structure of $\text{Sn}(\text{edt})_2(\text{apz})_2$ (Fig. 1) consists of discrete, monomeric, *trans*-octahedral units, with the tin atom at the centre of symmetry and monodentate apz ligands bonded through the imino

TABLE 1. Structure determination summary

<i>Crystal data</i>	
Empirical formula	C ₁₀ H ₁₈ N ₆ S ₄ Sn
Color; habit	colorless; transparent parallelepipeds
Crystal size (mm)	0.15 × 0.25 × 0.20
Crystal system	monoclinic
Space group	C2/c
Unit cell dimensions	
<i>a</i> (Å)	13.122(2)
<i>b</i> (Å)	11.216(2)
<i>c</i> (Å)	11.810(2)
β (°)	98.47(2)
Volume (Å ³)	1719.2(4)
<i>Z</i>	4
Formula weight	469.2
Density (calc.) (Mg/m ³)	1.813
Absorption coefficient (mm ⁻¹)	1.97
<i>F</i> (000)	936
<i>Data collection</i>	
Diffractometer used	Siemens R3m/V
Radiation	Mo K α ($\lambda = 0.71073$ Å)
Temperature (K)	294
Monochromator	highly oriented graphite crystal
2 θ Range (°)	4.5–60.0
Scan type	ω -2 θ
Scan speed	variable; 4.51 to 14.65°/min in ω
Standard reflections	2 measured every 150 reflections
Index ranges	–10 < <i>h</i> < 18, –12 < <i>k</i> < 15, –16 < <i>l</i> < 16
Reflections collected	5054
Independent reflections	2527 ($R_{int} = 3.33\%$)
Observed reflections	2127 ($F > 4.0\sigma(F)$)
<i>Solution and refinement</i>	
System used	Siemens SHELXTL PLUS (Release 4.1) (1987)
Refinement method	full-matrix least-squares
Quantity minimized	$\sum w(F_o - F_c)^2$
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.0109F^2$
No. parameters refined	133
Final <i>R</i> indices (obs. data) (%)	$R = 2.42$, $R_w = 3.36$
<i>R</i> indices (all data) (%)	$R = 2.96$, $R_w = 4.83$
Goodness-of-fit	0.31
Data-to-parameter ratio	16.0:1

TABLE 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{\AA}^2 \times 10^3$)

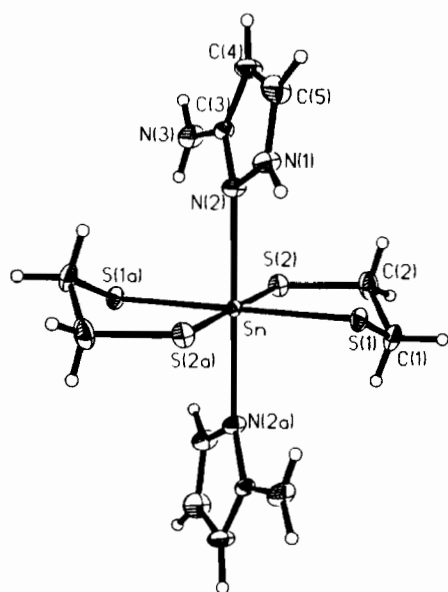
	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ^a
Sn	2500	2500	0	23(1)
S(1)	3311(1)	4466(1)	–76(1)	31(1)
S(2)	4187(1)	1678(1)	900(1)	32(1)
N(1)	2749(2)	2964(2)	–2663(2)	36(1)
N(2)	2867(1)	2080(2)	–1862(1)	30(1)
N(3)	3605(2)	143(2)	–1762(2)	40(1)
C(1)	4370(2)	4163(2)	1062(2)	36(1)
C(2)	4957(2)	3026(2)	871(2)	41(1)
C(3)	3398(2)	1225(2)	–2309(2)	28(1)
C(4)	3613(2)	1565(2)	–3393(2)	40(1)
C(5)	3180(3)	2670(2)	–3575(2)	42(1)

^aEquivalent isotropic *U* defined as one third of the trace of the orthogonalized *U*_{*ij*} tensor.

nitrogen N(2), as found in analogous tin(IV) complexes with monodentate diazole ligands [2]. Previously apz was considered bidentate in complexes of MCl₂ metal chlorides (M = Co, Ni, Cu, Zn, Cr, Hg) [8]. The planar apz ligands are roughly orthogonal (85.8°) to the five-membered SnS₂C₂ mean planes, which have a twist-envelope form with C(1) displaced by 0.74 Å out of the mean planes of the other four atoms. The Sn–S and the Sn–N bond distances (2.455(1) and 2.487(1), and 2.367(2) Å, respectively) are in agreement with the values reported for the corresponding complexes of Sn(edt)₂ with pyridine (2.463(3) and 2.467(3), and 2.390(6) Å, respectively) and 2-(2-pyridyl)ethylamine (2.467(1) and 2.478(1), and 2.374(3) Å, respectively) [3]. Comparison of the apz complex with the pyridine one (Fig. 2) shows that the inner core of the coordination

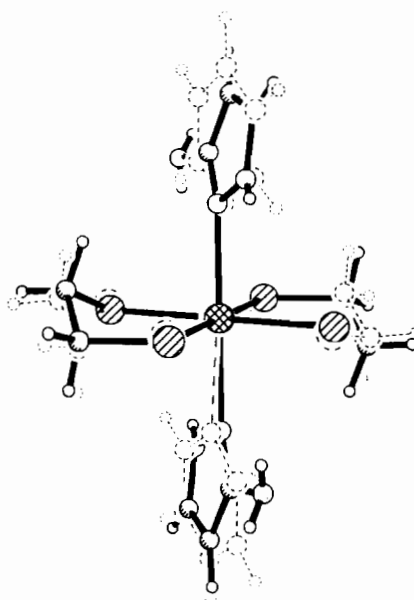
TABLE 3. Bond lengths (Å) and bond angles (°)

Sn–S(1)	2.455(1)	S(1)–Sn–S(2)	89.2(1)
Sn–S(2)	2.487(1)	S(1)–Sn–N(2)	89.8(1)
Sn–N(1)	2.367(2)	S(2)–Sn–N(2)	91.9(1)
S(1)–C(1)	1.818(2)	S(2)–Sn–S(1A)	90.8(1)
S(2)–C(2)	1.821(3)	N(2)–Sn–S(1A)	90.2(1)
N(1)–N(2)	1.363(3)	N(2)–Sn–S(2A)	88.1(1)
N(1)–C(5)	1.330(4)	Sn–S(1)–C(1)	95.3(1)
N(2)–C(3)	1.338(3)	Sn–S(2)–C(2)	98.4(1)
N(3)–C(3)	1.383(3)	Sn–N(2)–N(1)	118.8(1)
C(1)–C(2)	1.524(3)	Sn–N(2)–C(3)	134.3(1)
C(4)–C(3)	1.404(3)	N(1)–N(2)–C(3)	105.1(2)
C(5)–C(4)	1.367(4)	N(2)–N(1)–C(5)	111.3(2)
		S(1)–C(1)–C(2)	113.3(2)
		S(2)–C(2)–C(1)	113.5(2)
		N(1)–C(5)–C(4)	108.3(2)
		C(3)–C(4)–C(5)	104.8(2)
		N(2)–C(3)–N(3)	121.5(2)
		N(2)–C(3)–C(4)	110.5(2)
		N(3)–C(3)–C(4)	127.8(2)

Fig. 1. ORTEP plot of $[\text{Sn}(\text{edt})_2(\text{apz})_2]$ with thermal ellipsoids at the 40% probability level.

sphere is practically superimposable, the weighted r.m.s. deviation being 0.14 Å, and, as found in the pyridine and 2-(2-pyridyl)ethylamine complexes, there are no unusually short intermolecular contacts between the well separated monomers.

The IR spectrum shows the Sn–S symmetric and asymmetric stretching vibration absorption frequencies at 342 and 313 cm^{-1} , respectively, close to those found for similar complexes [3]. The N–H stretching absorption region presents two sharp bands at 3370 and 3289 cm^{-1} superimposed to a broad band centered at 3195 cm^{-1} . This pattern is not much different from that exhibited by the free ligand, having a strong broad band centered

Fig. 2. Superimposition of $[\text{Sn}(\text{edt})_2(\text{apz})_2]$ (full line) with $[\text{Sn}(\text{edt})_2(\text{py})_2]$ (dashed line).

at 3200 cm^{-1} with two shoulders at 3317 and 3395 cm^{-1} , and could be compatible with the presence of free and hydrogen-bonded N–H. But this should be excluded by the X-ray diffraction results, the shortest $\text{S}\cdots\text{H}$ contacts being $\text{S}(1)\cdots\text{H}(3)$ (hydrogen to N(3) at $\frac{1}{2}-x, \frac{1}{2}-y, -z$) and $\text{S}(2)\cdots\text{H}(2)$ (hydrogen to N(3) at $x, 1-y, z-\frac{1}{2}$), with distances of 2.87 and 2.82 Å and angles $\text{S}\cdots\text{H}-\text{N}$ of 137 and 148°, respectively. On the other hand, inter- and intra-molecular N–H \cdots X (X=Cl, Br) hydrogen bonding, evidenced by X-ray diffraction analysis and/or inferred by IR N–H frequencies, is a common feature of both *trans*-octahedral and trigonal bipyramidal complexes of diazole ligands with inorganic, SnX_4 [9], and metallorganic, R_2SnX_2 [2], tin(IV) substrates.

Supplementary material

Additional data, including anisotropic temperature factors (Table A), hydrogen atoms coordinates (Table B), and listing of observed/calculated structure factors (Table C), are available from the authors.

References

- 1 S. Trofimenko, *Prog. Inorg. Chem.*, **34** (1986) 115.
- 2 G. Bandoli, A. Dolmella, V. Peruzzo and G. Plazzogna, *J. Organomet. Chem.*, **452** (1993) 47, and refs. therein.
- 3 G. Bandoli, A. Dolmella, V. Peruzzo and G. Plazzogna, *Inorg. Chim. Acta*, **193** (1992) 185.

- 4 Y. Farhangi, *Inorg. Chim. Acta*, 129 (1987) 7.
- 5 F.A. Walker, D. Reis and V.L. Balke, *J. Am. Chem. Soc.*, 106 (1984) 6888.
- 6 N. Bodor, M.J.S. Dewar and A.J. Harget, *J. Am. Chem. Soc.*, 92 (1970) 2929.
- 7 M. Bruix, T. De Mendoza, R.M. Claramunt and J. Elguero, *Magn. Reson. Chem.*, 3 (1985) 367.
- 8 B. Banerjee, S.K. Nandi, J. Roy Chaudhuri and Bismansh Sur, *Indian J. Chem.*, 22A (1983) 857.
- 9 I.R. Masguer, E. Freijanes, J. Sordo, J.S. Casas and R.M. Bermejo, *Inorg. Chim. Acta*, 25 (1977) 203.