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An adduct of aquadichlorodiphenyltin(IV) and 4,4,8,8-tetrakis(1-pyrazolyl)pyrazabole†

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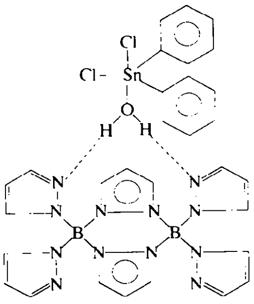
Abstract

In $[SnCl_2(C_6H_5)_2(H_2O)]\cdot C_{18}H_{18}B_2N_{12}$, a hydrogen-bonded adduct of aquadichlorodiphenyltin(IV) and 4,4,8,8-tetrakis(1-pyrazolyl)pyrazabole, the central $B(N_2)_2B$ ring of the pyrazabole unit exists in a boat conformation. The $Ph_2Sn(H_2O)Cl_2$ unit exhibits a distorted trigonal-bipyramidal coordination geometry around tin, with one long and one short Sn—Cl bond [2.4686 (14) and 2.338 (2) Å, respectively]. Two phenyl groups and one Cl atom occupy the trigonal plane, and the other Cl atom and the coordinated water molecule occupy the axial positions.

Comment

Poly(1-pyrazolyl)borate ions of the general formula $[R_nB(pz^*)_{4-n}]^-$ (pz* = pyrazole or C-substituted pyrazole; *R* = H or other non-coordinating substituent; *n* = 0–2) have been widely used as chelating ligands in transition and main group metal chemistry (Trofimenko, 1986, 1992; Niedenzu & Trofimenko, 1986; Lobbia *et al.*, 1995, 1996; Dey *et al.*, 1997). However, studies on the coordinating ability of neutral species containing a terminal $B(pz)_2$ group in 4,4-bis(1-pyrazolyl)pyrazaboles such as $R_2B(\mu\text{-pz})_2B(pz)_2$ (*R* = H, Et), $(Me_2N)(pz)B(\mu\text{-pz})_2B(pz)_2$ and 4,4,8,8-tetrakis(1-pyrazolyl)pyrazabole, *i.e.* $(pz)_2B(\mu\text{-pz})_2B(pz)_2$, have received scant attention, except for a very few examples. These include the preparation and spectral reports of the complexes $[R_2B(\mu\text{-pz})_2B(\mu\text{-pz})_2]ZnCl_2$, $Cl_2Zn(\mu\text{-pz})_2B(\mu\text{-pz})_2B(\mu\text{-pz})_2ZnCl_2$, $(pz)_2B(\mu\text{-pz})_2B(\mu\text{-pz})_2(\eta^3\text{-CH}_2CR'CH_2Pd)$ and $(\eta^3\text{-CH}_2CR'CH_2Pd)(\mu\text{-pz})_2B(\mu\text{-pz})_2B(\mu\text{-pz})_2(\eta^3\text{-CH}_2CR'CH_2Pd)$ (*R'* = Me, Ph) (Bielawski *et al.*, 1986). However, no solid-state molecular structure determined by X-ray crystallography has been reported for any of the above compounds, which would unambiguously prove the coordination of the terminal $B(pz)_2$ group to the metal species, particularly $ZnCl_2$. Our interest in the reactivities of pyrazole derivatives of boron with organotin(IV) compounds (Dey *et al.*, 1997) has led us to investigate the reactivity of neutral species containing a terminal $B(pz)_2$ group, *viz.* $(pz)_2B(\mu\text{-pz})_2B(pz)_2$, towards diphenyltin dichloride, Ph_2SnCl_2, to see whether complexation through the terminal $B(pz)_2$ group takes place. Instead, an unexpected adduct, (I), of aquadichlorodiphenyltin(IV) and 4,4,8,8-tetrakis(1-pyrazolyl)pyrazabole was isolated. We present here the results of the X-ray crystal structure determination of (I).



(I)

In the title compound, the central B_2N_4 ring of the pyrazabole molecule adopts a boat conformation as in free $(pz)_2B(\mu\text{-pz})_2B(pz)_2$ (Brock *et al.*, 1985), with pseudo-axial and pseudo-equatorial terminal pyrazolyl groups. However, the B—N bond lengths here are slightly different from those in the free molecule, which may be due to the presence of $Ph_2Sn(H_2O)Cl_2$ in the crystal lattice. This difference in the environment around boron is also reflected in the ^{11}B NMR spectrum. This compound shows a $\delta(^{11}B)$ value of 1.35 (in $CHCl_3$) *versus* 0.7 p.p.m. (in CD_3CN) for free $(pz)_2B(\mu\text{-pz})_2B(pz)_2$ (Layton *et al.*, 1985). However, the N—B—N angles are quite similar to those of the parent $(pz)_2B(\mu\text{-pz})_2B(pz)_2$. All C—C and N—N bond lengths are normal.

The $Ph_2Sn(H_2O)Cl_2$ molecule adopts a distorted trigonal-bipyramidal coordination geometry around tin in which two phenyl groups and one Cl atom (Cl2) occupy the equatorial positions, and the two axial positions are occupied by oxygen (O1) and the other Cl atom (Cl1). The distortion is illustrated by the deviation

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† Alternative name: aquadichlorodiphenyltin(IV)–4,4,8,8-tetrakis(1-pyrazolyl)-3a,4a,7a,8a-tetraaza-4,8-dibora-*s*-indacene (1/1).

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of the axial O1—Sn—Cl1 bond angles [172.27 (10)°] from linearity. This is also documented by the narrowed C19—Sn—Cl2 and C25—Sn—Cl2 angles of 117.6 (2) and 117.8 (2)°, respectively, and by the widened C19—Sn—C25 angle of 123.1 (2)°, compared with a value of 120° for an ideal trigonal plane. The Sn atom is slightly displaced from the plane through atoms Cl2, C19 and C25, by 0.158 (1) Å towards Cl1.

The axial Sn—Cl bond length [2.4686 (14) Å] is considerably longer than the equatorial Sn—Cl bond length [2.338 (2) Å]. The long Sn—O bond [2.304 (3) Å] may be due to its partial ionic character, similar features having been observed in the structures of $SnMe_2Cl_2 \cdot H_2O \cdot$[Ni{*N*,*N*′-bis(3-methoxysalicylidene)ethylenediamine}] and $SnMe_2Cl_2 \cdot H_2O \cdot$[Ni{*N*,*N*′-bis(3-methoxysalicylidenepropane)-1,2-diamine}] (Cunningham *et al.*, 1993). The Cl—Sn—Cl, Cl—Sn—O, C—Sn—O and C—Sn—Cl bond angles in (I) are comparable with those observed in the above structures. The Sn—C(Ph) bond lengths are comparable with those in other organotin compounds (Khoo *et al.*, 1987; Fun *et al.*, 1991). The water O atom makes short contacts of 2.784 (7) and 2.847 (6) Å with atoms N8 and N10, respectively. Although the water H atoms were not found, the presence of hydrogen-bonding contacts (which results in the formation of the hydrogen-bonded adduct) can be confirmed from the angle subtended at the water oxygen [124.0 (2)°] by these short contacts.

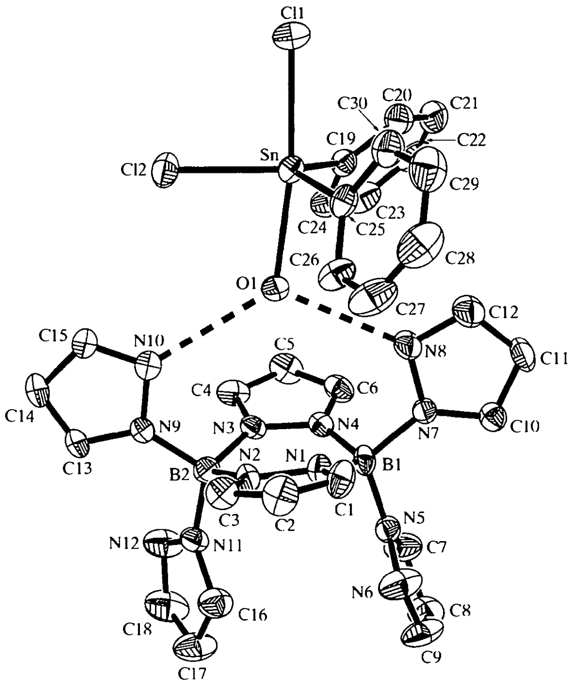

Fig. 1. The structure of the title compound showing 30% probability displacement ellipsoids and the atom-numbering scheme. H atoms have been omitted for clarity.

Experimental

The title compound was prepared by the reaction of 4,4,8,8-tetrakis(1-pyrazolyl)pyrazabole (1.06 g, 2.50 mmol) and Ph_2SnCl_2 (1.72 g, 5.00 mmol) in dry benzene (80 ml). The reaction mixture was heated under reflux for 8 h and filtered. Evaporation of the solvent followed by recrystallization from chloroform/*n*-pentane afforded the title compound. Suitable single crystals were obtained from a chloroform/*n*-pentane (1:1 *v*/*v*) mixture below ambient temperature [yield: 1.16 g (60%); m.p. 438–439 K]. Analysis found: C 45.48, H 3.72, N 21.56, B 2.82, Sn 15.18%; calculated for $C_{30}H_{30}B_2Cl_2N_{12}OSn$: C 45.85, H 3.85, N 21.39, B 2.75, Sn 15.10%; IR (KBr disc): ν 3500–1700 cm^{-1} (broad envelope, H_2O); ^1H NMR ($CDCl_3$): δ 3.50 (broad *s*, 2H, H_2O), 6.08 (*t*, 4H, C4—H of terminal pz groups), 6.60 (*t*, 2H, C4—H of bridging pz groups), 6.75 (*d*, 4H, C3/C5—H of bridging pz groups), 7.33–7.83 (*m*, 18H, phenyl and C3/C5—H of terminal pz groups); ^{11}B NMR ($CHCl_3$): δ 1.35; ^{119}Sn NMR ($CHCl_3$): δ −51.5.

Crystal data

$[SnCl_2(C_6H_5)_2(H_2O)] \cdot$-
$C_{18}H_{18}B_2N_{12}$
$M_r = 785.87$
Orthorhombic
$Pna2_1$
$a = 23.930 (2)$ Å
$b = 12.5245 (11)$ Å
$c = 11.903 (2)$ Å
$V = 3567.5 (7)$ Å^3
$Z = 4$
$D_x = 1.463$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 39 reflections
$\theta = 5.34$–$12.45°$
$\mu = 0.909$ mm^{-1}
$T = 293 (2)$ K
Plate
0.62 × 0.46 × 0.26 mm
Colourless

Data collection

Siemens *P*4 diffractometer
$\theta/2\theta$ scans
Absorption correction:
ψ scan (Siemens, 1994)
$T_{min} = 0.398$, $T_{max} = 0.790$
5328 measured reflections
4678 independent reflections
3164 reflections with $I > 2\sigma(I)$

$R_{int} = 0.043$
$\theta_{max} = 27.49°$
$h = -1 \rightarrow 31$
$k = -1 \rightarrow 16$
$l = -1 \rightarrow 15$
3 standard reflections every 97 reflections intensity decay: <3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.088$
$S = 0.887$
4678 reflections
433 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0373P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.62$ e Å^{-3}
$\Delta\rho_{min} = -1.00$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = 0.01 (3)

Table 1. *Selected geometric parameters (Å, °)*

Sn—Cl1	2.4686 (14)	Sn—C19	2.121 (7)
Sn—Cl2	2.338 (2)	Sn—C25	2.123 (6)
Sn—O1	2.304 (3)		

C19—Sn—C25	123.1 (2)	O1—Sn—Cl2	82.30 (11)
C19—Sn—O1	86.6 (3)	C19—Sn—Cl1	94.9 (2)
C25—Sn—O1	88.6 (2)	C25—Sn—Cl1	96.9 (2)
C19—Sn—Cl2	117.6 (2)	O1—Sn—Cl1	172.27 (10)
C25—Sn—Cl2	117.8 (2)	Cl2—Sn—Cl1	90.31 (6)

The title structure was solved by direct methods and refined by full-matrix least-squares techniques. All non-water H atoms were located from a difference Fourier map, idealized and allowed to ride on their carrier atoms. The maximum and minimum ΔF extremes were found at 0.97 and 1.04 Å, respectively, from the Sn atom. The poor agreement between expected and reported transmission-factor ranges is partly attributed to the absence of suitably strong reflections near $\chi = 90°$ which could be utilized for ψ-scan measurements.

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXL93* and *PARST* (Nardelli, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1258). Services for accessing these data are described at the back of the journal.

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Bis(3,5-dimethylpyrazole-*N*^{2})bis(thiocyanato-*N*)cobalt(II) monohydrate

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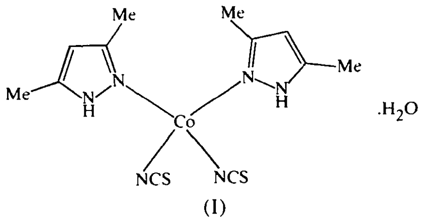
Abstract

In the title compound, [Co(NCS)$_2$(C$_5$H$_8$N$_2$)$_2$]·H$_2$O, the metal atom exhibits an approximately tetrahedral configuration. The Co—N bond distances and N—Co—N bond angles are in the ranges 1.936 (3)–2.010 (3) Å and 101.6 (1)–113.7 (2)°, respectively. The water molecule is involved in O—H···S and N—H···O hydrogen bonds, which result in the formation of an infinite chain parallel to the *c* axis.

Comment

Extensive investigations have been carried out on imidazole derivatives of cobalt(II) complexes containing thiocyanate (Maslejova *et al.*, 1997). In order to investigate the influence of steric properties on the stoichiometry as well as on the stereochemistry of the resulting species, some complexes of the isomeric pyrazoles have been studied. Although the title complex, (I), has been prepared previously (Anagnostopoulos, 1976) and some of its physical properties described (Bagley *et al.*, 1970), its crystal structure has not, to our knowledge, been reported before now.



(I)

The Co atom is tetrahedrally coordinated by four N atoms, two from the monodentate thiocyanate groups and the others from the two 3,5-dimethylpyrazole ligands, building up the CoN$_4$ chromophore. The

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