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Supplementary data for this paper are available from the IUCr electronic archives (Reference: KA1268). Services for accessing these data are described at the back of the journal.

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catena-Poly[(dichlorodimethyltin)-μ-(4,4′-bipyridine-*N*:*N*′)]

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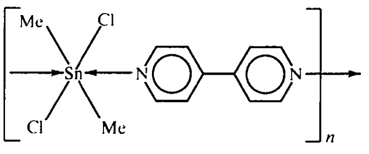
Abstract

The 4,4′-bipyridine moiety in the title compound, $[SnCl_2(CH_3)_2(C_{10}H_8N_2)]_n$, bridges adjacent dichlorodimethyltin molecules to form a linear chain, whose six-coordinate Sn atom exists in an all-*trans* O_h geometry.

Comment

Dimethyltin dichloride (Davies *et al.*, 1970) forms a 2:1 complex with pyrazine, regardless of the stoichiometry of the reactants, when the reaction is carried out in an anhydrous solvent. The centrosymmetric $[(CH_3)_2SnCl_2]_2.C_4H_4N_2$ complex is five-coordinate, but the trigonal-bipyramidal geometry of the Sn atom is distorted towards an octahedron owing to a tin–chlorine bridge, which connects adjacent molecules into a linear chain. The crystal structure also features an unusually long Sn—N bond [*cf.* 2.746 (8) (Rivarola *et al.*, 1987) and 2.746 (6) Å (Cunningham *et al.*, 1988)]. Reactions of the Lewis acceptor with ligands having two basic nitrogen sites sometimes yield dimeric tetramethyldichlorodistannoxane; aminomethyl-2-pyridine catalyzes the hydrolysis of dimethyltin dichloride in moist solvents (Crowe *et al.*, 1979), as does pyrazine (Cunningham *et al.*, 1988). The Sn—N bond in the 2:1 complex is longer than that [2.62 (1) Å] in $[(CH_3)_2ClSn(CH_2)SnCl(CH_3)_2]_2.C_4H_4N_2$ (Austin *et al.*, 1987); the Lewis acidity of tin in this tetranuclear triorganotin complex is much reduced compared with that of dimethyltin chloride. Curiously, pyrazine furnishes an unambiguously six-coordinate 1:1 complex with dimethyltin dibromide in which the bond dimensions involving the Sn atom are normal (Rivarola *et al.*, 1987).

The 4,4′-bipyridine complex with dimethyltin dichloride, (I), which was synthesized in 95% ethanol, shows no evidence of decomposition when exposed to air. The Sn atom is six-coordinate in an all-*trans* octahedral geometry. The Sn—N bond distance [Sn—N 2.402 (2) Å] is similar to that [2.40 (1) Å] found in $[(CH_3)_2SnBr_2].C_4H_4N_2$ (Rivarola *et al.* 1987), but is somewhat longer than those found in the 1:2 complexes with monodentate imidazole [2.312 (2) Å; Martinez *et al.*, 1990] and *N*-methylimidazole [2.329 (5) Å; Bardi *et al.*, 1984], as well as those [2.29 (1) and 2.32 (1) Å] found in the chelated dimethyltin dibromide complex of *N*,*N*′-dimethyl-2,2′-biimidazole (Lopez *et al.*, 1992). The 4,4′-bipyridine moiety is flat, the two pyridyl rings being constrained by symmetry to be coplanar.



(I)

Although 4,4′-bipyridine has been extensively used in transition metal chemistry for the construction of chains, rectangular grids and cages (Tong, Cai *et al.*, 1998; Tong, Ye *et al.*, 1998), its use in main-group chemistry appears to be limited; the first structural account of a tin complex describes the isostructural 2:1 tri-*p*-tolyltin halide complexes in which the 4,4′-bi-

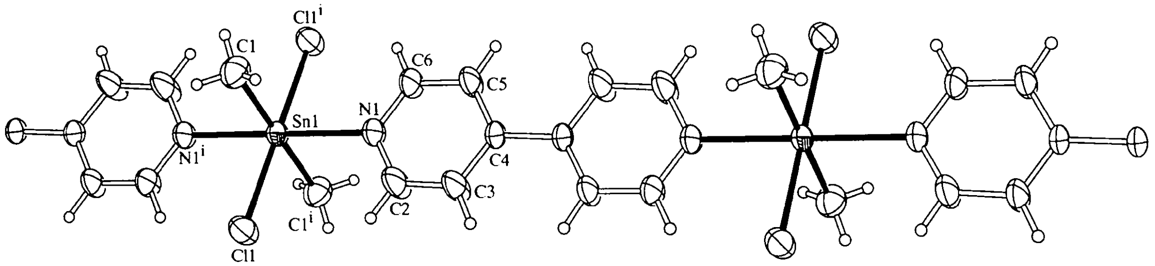


Fig. 1. *ORTEP*II (Johnson, 1976) plot of the title polymeric chain at the 50% probability level. H atoms are drawn as spheres of arbitrary radii.

pyridine ligand bridges two tri-*p*-tolyltin halide entities [Sn—N 2.668 (3) Å for the chloride, 2.653 (3) Å for the bromide and 2.655 (7) Å for the iodide; Bajur *et al.*, 1992].

Experimental

Dimethyltin dichloride and 4,4′-bipyridine (1:1 molar ratio) were heated in a large volume of 95% ethanol. The title adduct separated as large crystals on cooling the filtered solution.

Crystal data

$[SnCl_2(CH_3)_2(C_{10}H_8N_2)]$
$M_r = 375.84$
Monoclinic
$P2_1/c$
$a = 6.5478\ (2)$ Å
$b = 9.9048\ (3)$ Å
$c = 10.8386\ (4)$ Å
$\beta = 95.791\ (4)°$
$V = 699.35\ (4)$ Å^3
$Z = 2$
$D_x = 1.785$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 12.0$–$13.0°$
$\mu = 2.188$ mm^{-1}
$T = 298\ (2)$ K
Block
$0.45 \times 0.40 \times 0.35$ mm
Colorless

Data collection

Enraf–Nonius CAD-4 diffractometer
ω scans
Absorption correction: ψ scans (North *et al.*, 1968)
$T_{min} = 0.374$, $T_{max} = 0.465$
2189 measured reflections
2030 independent reflections

1750 reflections with $I > 2\sigma(I)$
$R_{int} = 0.008$
$\theta_{max} = 29.97°$
$h = 0 \rightarrow 9$
$k = 0 \rightarrow 13$
$l = -15 \rightarrow 15$
3 standard reflections
frequency: 60 min
intensity decay: 3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.023$
$wR(F^2) = 0.061$
$S = 1.019$
2030 reflections
91 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0345P)^2 + 0.3492P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.448$ e Å^{-3}
$\Delta\rho_{min} = -0.409$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Sn1—C1	2.115 (3)	Sn1—N1^i	2.402 (2)
Sn1—C1^i	2.115 (3)	Sn1—Cl1	2.569 (1)
Sn1—N1	2.402 (2)	Sn1—Cl1^i	2.569 (1)
C1—Sn1—N1	91.2 (1)	C1^i—Sn1—Cl1	89.6 (1)
C1—Sn1—N1^i	88.8 (1)	C1^i—Sn1—Cl1^i	90.4 (1)
C1—Sn1—Cl1	90.4 (1)	N1—Sn1—Cl1	89.3 (1)
C1—Sn1—Cl1^i	89.6 (1)	N1—Sn1—Cl1^i	90.7 (1)
C1^i—Sn1—N1	88.8 (1)	N1^i—Sn1—Cl1	90.7 (1)
C1^i—Sn1—N1^i	91.2 (1)	N1^i—Sn1—Cl1^i	89.3 (1)

Symmetry code: (i) $-x, -y, -z$.

Methyl H atoms were located and refined with the three C—H distances set to be equal to each other by a *SADI* instruction in *SHELXL*97 (Sheldrick, 1997*a*). Aromatic H atoms were allowed to ride on their parent C atoms with $U(H) = 1.5U_{eq}(C)$.

Data collection: *CAD*-4/*PC* (Kretschmar, 1994). Cell refinement: *CELDIM* in *CAD*-4 *VAX*/*PC* (Enraf–Nonius, 1988). Data reduction: *XCAD*4 (Harms, 1997). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997*b*). Program(s) used to refine structure: *SHELXL*97. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1191). Services for accessing these data are described at the back of the journal.

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Bis[μ-(di-2-pyridyl ketone thiosemicarbazonato-N^1,N'',S:N')]bis[(isothiocyanato-N)-copper(II)] Bis(dimethylformamide) Solvate

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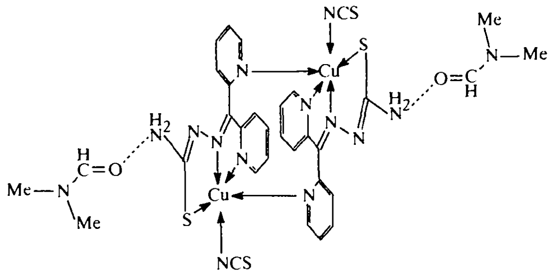
Abstract

In the title compound, $[Cu_2(NCS)_2(C_{12}H_{10}N_5S)_2].2C_3H_7NO$, derived from the tetradentate ligand di-2-pyridyl ketone thiosemicarbazone, the coordination geometry about each Cu^{II} atom is distorted square pyramidal, with one pyridine N atom, the S atom and the imino N atom from the thiosemicarbazone ligand, together with the N atom from an isothiocyanato ligand, in the basal plane; a pyridyl N atom of an adjacent moiety occupies the apical position, serving as a bridge to form a centrosymmetric dimeric structure.

Comment

Thiosemicarbazones belong to a large group of thiourea derivatives, the biological activities of which are a function of the parent aldehyde or ketone (Podhye & Kauffman, 1985; Liberta & West, 1992). A number of thiosemicarbazones and their copper and iron compounds have also been found to be active in cell destruction, as well as in the inhibition of DNA synthesis (West *et al.*, 1993; Liu *et al.*, 1995). We report here the crystal structure of a new copper(II) thiosemicarbazone complex, (I).



(I)

The title complex (Fig. 1) has a dimeric structure. The coordination geometry about the copper(II) ion is square pyramidal. The pyridine N4 atom, the imino N3 atom and the thiosemicarbazone S1 atom, together with the thiocyano N6 atom, comprise the basal plane, whereas the apical position is occupied by the pyridine N5($-x$, $1-y$, $-z$) atom of the symmetry-related half of the dimer. The basal plane shows appreciable tetrahedral distortion (mean deviation from the plane 0.15 Å), which deforms the square-pyramidal coordination polyhedron towards trigonal-bipyramidal geometry. The bond lengths in the basal plane agree well with those generally found in copper(II) complexes containing thiosemicarbazone derivatives acting as mononegative tridentate ligands (Farrarri *et al.*, 1989; Garcia-Tojal *et al.*, 1994).

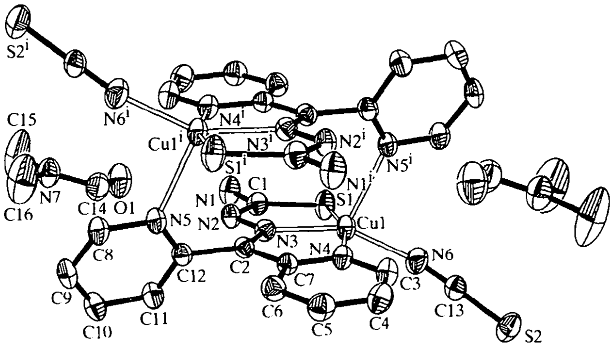


Fig. 1. View of the title compound. Displacement ellipsoids are shown at the 30% probability level. [Symmetry code: (i) $-x$, $1-y$, $-z$.]

While the thiosemicarbazone moiety in the 'free' ligand has an *E* configuration about both C2—N3 and C1—N2 (Duan *et al.*, 1996), the copper(II) complex has the *E* configuration about C2—N3, but a *Z* configuration about C1—N2, with the donors placed on the same