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Preliminary communication

Organotin-DMIT complexes: crystal structure of $[Bu_4N][Me_2SnCl(DMIT)]$

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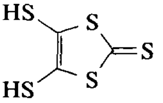
Abstract

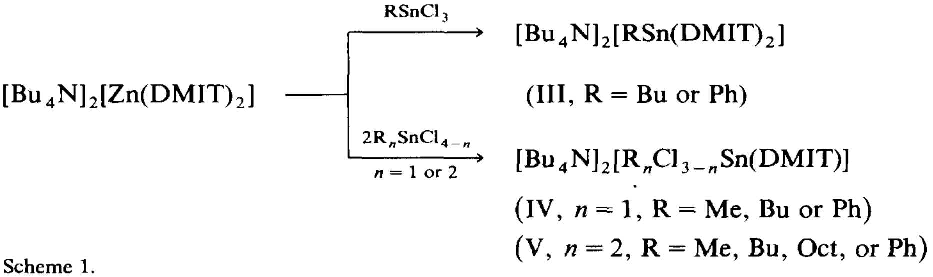
Various organotin-DMIT complexes have been prepared from organotin halides and $[Bu_4N]_2[Ni(DMIT)_2]$ (H_2-DMIT = 4,5-dimercapto-1,3-dithiole-2-thione). The crystal structure of $[Bu_4N][Me_2ClSn(DMIT)]$ (V, R = Me) is reported: the compounds contains a trigonal bipyramidal tin atom in the anion.

Several compounds of the ligand, DMIT [H_2-DMIT = 4,5-dimercapto-1,3-dithiole-2-thione (I)], have been studied; by far the majority of these have involved transition metals. Several of the transition metal complexes have interesting electrical properties [1–7], including some with superconducting abilities, e.g. $[Me_4N][Ni(DMIT)_2]_2$ at 5 K under 7 kbar pressure [8]. Main group compounds have been much less well studied, although some inorganic complexes have been prepared, for example of Zn, Cd and Hg, such as $[R_4N]_2[M(DMIT)_2]$ [9] and of In and Tl [10].



(I)

Recently we have prepared some novel organotin-DMIT compounds and we now wish to report our preliminary findings. The organotin complexes were obtained from reactions of R_nSnCl_{4-n} (n = 1 or 2) with II, M = Zn, R = Bu, Scheme 1:



Scheme 1.

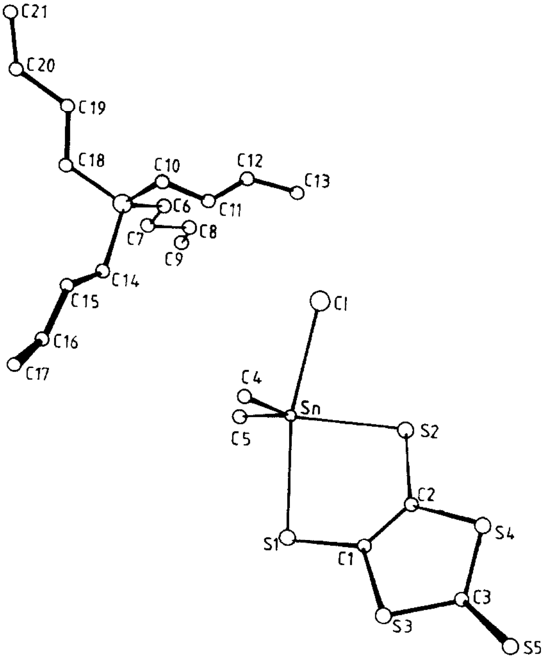


Fig. 1. Molecular structure of V, R = Me.

Attempts to replace Cl^- in IV or V by $[Et_2NCS_2]^-$ failed but halogen exchanges with I^- in EtOH did occur.

A crystal structure determination of V, R = Me, [11*] revealed it to contain trigonal bipyramidal Sn, with Cl and S(1) axial, in the anion (Fig. 1, Table 1) [12*]. The Sn–S and Sn–Cl bond lengths are in the regions usually found for such bonds; for example, values obtained for the related trigonal bipyramidal complex $[Et_4N][4\text{-}Me\text{-}2\text{-}SC_6H_3SSnPh_2Cl]$ (VI) are Sn–Cl(*ax*) 2.588(2), Sn–S(*ax*) 2.544(2) and Sn–S(*eq*) 2.436(2) Å [13]. The difference in the Sn–S bond lengths in V, R = Me, [2.451(3) and 2.622(3) Å], while being greater than that in VI, is appreciably less than that found in the trigonal bipyramidal neutral species $[Me_2ClSnS_2CNMe_2]$ (VII) [Sn–S(*ax*) 2.79(1) and Sn–S(*eq*) 2.48(a) Å [14]. The Me–Sn bond lengths [2,17(5) and 2.20(5) Å] and C–Sn–C bond angle [128(2)°] in VII are only slightly greater than the corresponding values in V, R = Me. The Mössbauer parameters of V, R = Me, are IS = 1.26 mm s^{-1} and QS = 2.48 mm s^{-1}. The QS values of pentacoordinate $Me_2SnCl(S_2CNR_2)$ compounds [$R_2 = Me_2$, Et_2, $(CH_2Ph)_2$ and $(CH_2)_4$] are between 2.72 and 2.98 mm s^{-1} [15] and that for VI is 2.08 mm s^{-1} [12]. Correlations have been attempted between C–Sn–C bond angles and QS values for dimethyltin species; the QS value for V, R = Me, is approximately in line with that expected for a C–Sn–C bond angle of 120.9(6)° [16].

Correlations have also been made between coupling constants $^1J(^{119}Sn-^{13}C)$ and $^2J(^{119}Sn-^1H)$ in the NMR spectra in solution with the C–Sn–C bond angles in the

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* Reference number with asterisk indicates a note in the list of references.

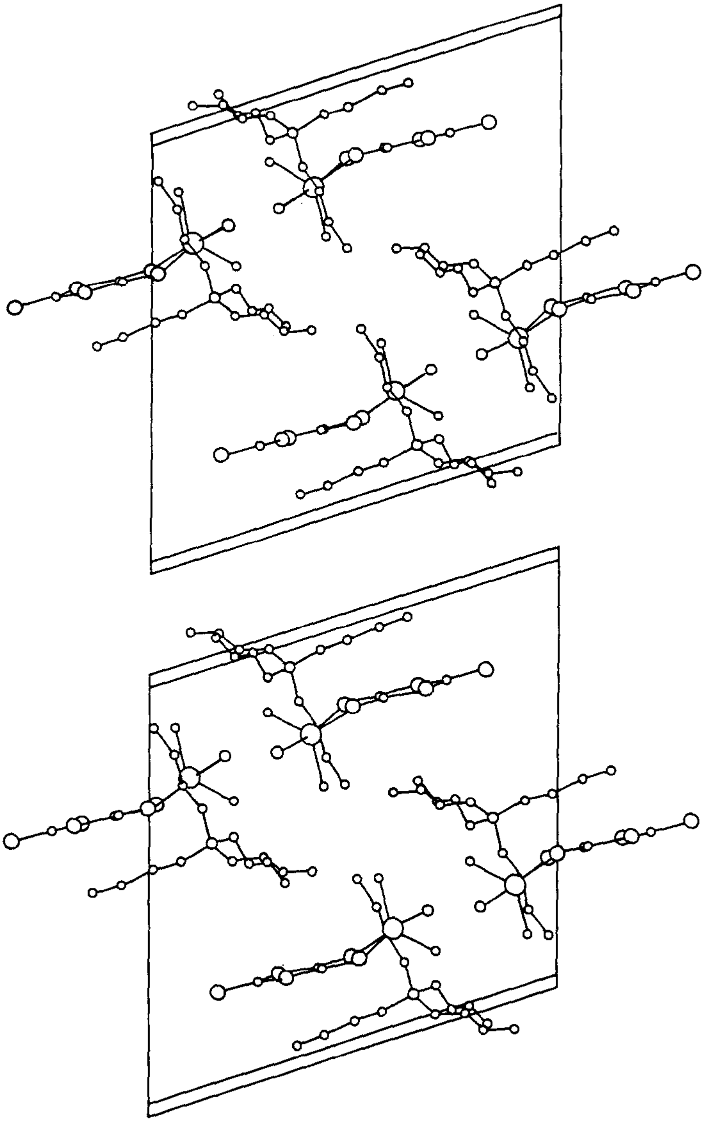

Fig. 2. Crystal structure of V, R = Me.

Table 1

Selected bond lengths (Å) and bond angles (°)

Sn–Cl	2.556(3)	Sn–S(2)	2.451(3)	Sn–S(1)	2.662(3)
Sn–C(4)	2.132(11)	Sn–C(5)	2.131(10)	C(3)–S(5)	1.630(12)
C(1)–C(2)	1.342(15)	C(1)–S(3)	1.748(11)	S(2)–C(2)	1.751(11)
Cl–Sn–S(2)	83.1(1)	Cl–Sn–S(1)	167.3(1)	Cl–Sn–C(4)	92.5(4)
Cl–Sn–C(5)	91.2(4)	C(4)–Sn–C(5)	120.9(6)	C(4)–Sn–S(1)	95.6(4)
C(4)–Sn–S(2)	118.2(4)	C(5)–Sn–S(1)	93.0(4)	C(5)–Sn–S(2)	120.8(4)

solid state for methyltin species [16]; J values for V, R = Me (549 and 74.2 Hz respectively) fit well the correlations for a value of C–Sn–C = 120.9(6)°.

All new complexes had analytical and spectral data in agreement with their structures.

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11 *Crystal data:* $C_{21}H_{42}ClNS_5Sn$: $M = 622.5$, monoclinic, space group $P2_1/n$, $a = 16.770(20)$, $b = 11.138(14)$, $c = 16.8601(20)$ Å, $\beta = 107.58(9)°$, $V = 3002(6)$ Å^3, $Z = 4$, $D_c = 1.34$ kg m^{-3}, $D_m = 1.32$ kg m^{-3}, $F(000) = 1288$, T = room temperature. No. of reflections 5269, of which 3002 had $F > 6\sigma(F)$, $R = 0.00654$ and $R_w = 0.0701$.

12 $[Bu_4N][Me_2SnCl(DMIT)]$, dark-orange crystals from ^{i}PrOH/$CHCl_3$, m.p. 115°C [ν_{max} ($CHCl_3$) 459.2 nm]. Analysis: Found: C, 40.31; H, 6.81; N, 2.21; S, 26.31. $C_{21}H_{42}NClS_5Sn$ calc.: C, 40.5; H, 6.8; N, 2.2; S, 25.71%. ^{1}H NMR ($CDCl_3$, 250 MHz) 1.16 (s, 6H, $J(^{119}Sn-^1H)$ 74.2 Hz, Me_2Sn); 1.04 (t, 12H, J 7.3 Hz), 1.46 (sextuplet, 8H, J 7.3), 1.65 (m, 8H) and 3.23 (m, 8H), Bu_4N; ^{13}C NMR ($CDCl_3$); 13.05 ($J(^{119}Sn-^{13}C)$ 569 Hz, Me_2Sn); 13.33, 19.37, 23.57 and 58.57 (Bu_4N); 131.66 (C=C), 207.91 (C=S); ^{119}Sn NMR ($CDCl_3$,), −24.66; IR (KBr) cm^{-1} 1057 and 1032 (C=S), 1441 (C=C), 548 and 517 (MeSn). Mössbauer: IS 1.26 mm s^{-1}, QS 2.48 mm s^{-1}. Γ 0.82.

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