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SYNTHESIS, SPECTROSCOPIC INVESTIGATION AND MOLECULAR STRUCTURE OF PENTACARBONYL-5-t-BUTYL-5-AZA-2,8-DITHIA-1-STANNOBICYCLO[3.3.$0^{1,5}$]OCTANECHROMIUM(0)

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Summary

The compound pentacarbonyl-5-t-butyl-5-aza-2,8-dithia-1-stannobicyclo-[3.3.$0^{1,5}$]octanechromium(0) was prepared in good yield by the reaction of 5-t-butyl-5-aza-2,8-dithia-1-stannobicyclo[3.3.$0^{1,5}$]octane with $Cr(CO)_6$ in THF under UV-irradiation. The crystal and molecular structure was determined from three-dimensional X-ray data. The crystals are monoclinic, space group $P2_1/c$. The unit cell, with dimensions a 14.963(9), b 10.026(5), c 13.565(5)Å, β 114.68°(5), contains 4 molecules. The structure was solved by the Patterson-method. The full-matrix refinement with the 2734 independent reflexions gave a final R value of 0.034. The eight-membered ring adopts an asymmetric boat-boat conformation with a tin–nitrogen bond length of 2.40 Å; the tin–chromium bond length is 2.62 Å.

Introduction

Recently we reported the tin(II)-containing bicyclic octanes of the general type $Sn(XCH_2CH_2)_2Y$ with X = O, S and Y = NR, PR, O and S [1–3]. These compounds show a more or less strong tin–Y interaction, the strength depending on the nature of the heteroatoms X and Y. Our objective was to investigate the behaviour of these compounds as complexing ligands for transition metals and the influence of that complexation on the Sn–Y bond strength.

Results and discussion

The reaction of 5-t-butyl-5-aza-2,8-dithia-1-stannobicyclo[3.3.$0^{1,5}$]octane with chromium hexacarbonyl gave the corresponding tin(II)-substituted transition metal

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TABLE 1

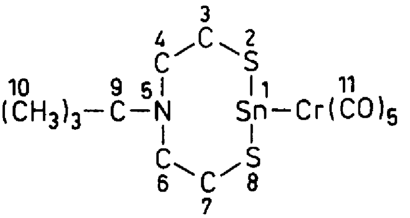
^1H, ^{13}C AND ^{119}Sn NMR DATA IN $CDCl_3$ AT *T* 301 K

Nucleus	Chemical shifts (ppm)					
	1	3/7	4/6	9	10	11
^1H		3.05/3.17	3.35		1.55	
^{13}C		32.5	58.7	64.0	29.0	217.5
^{119}Sn	622.8					

complex in high yield (eq. 1, 2).

$$Cr(CO)_6 \xrightarrow[-CO]{THF,\,h\nu} Cr(CO)_5 \cdot THF \tag{1}$$

$$Cr(CO)_5 \cdot THF + Sn(SCH_2CH_2)_2NBu^t \xrightarrow[-THF]{} Bu^tN(CH_2CH_2S)_2SnCr(CO)_5 \tag{2}$$



The complex is a yellow, air-stable, crystalline solid and is monomeric in benzene. The ^1H NMR spectrum is temperature dependent and indicates the existence of a dissociation–inversion process for the complexed as for the free ligand (see Table 1) [2,3]. The ^{13}C NMR spectrum shows the equivalence of the 3 and 7 carbon atoms and also of the 4 and 6 carbon atoms (Table 1). The broadening of the ^{13}C NMR signal of C(10) is consistent with a hindered rotation of the butyl group attached to the nitrogen atom. In the ^{119}Sn NMR spectrum there is a signal at very low field compared to that for the free ligand. This effect has been noticed in tin(II) halide complexes of transition metals [4].

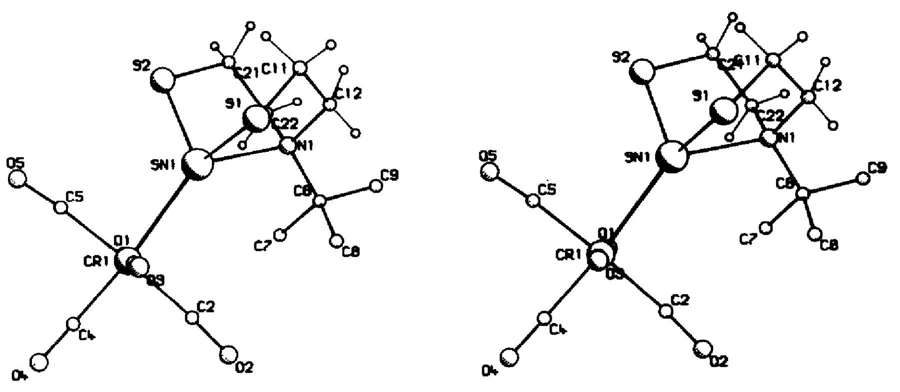


Fig. 1. Geometry of the complex and numbering of the atoms.

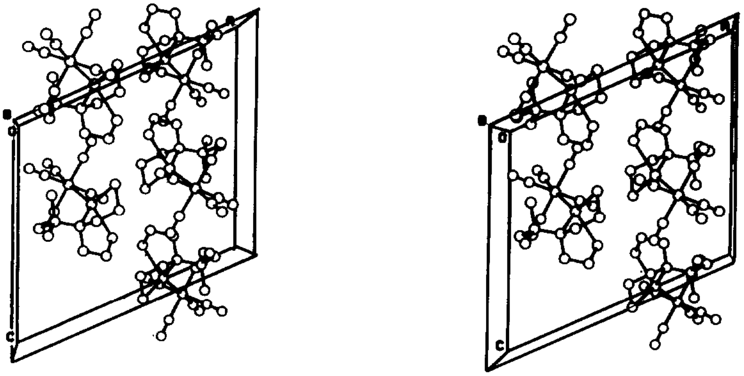


Fig. 2. The unit-cell packing.

There are four IR absorptions for the carbonyl fragment ($A_1^{(2)}$, 2050; B_1, 1972; $A_1^{(1)}$ 1948; E 1910 cm^{-1}) indicating a distorted C_{4v} symmetry.

TABLE 2

FRACTIONAL ATOMIC COORDINATES ($\times 10^4$, $\times 10^3$ for H)

	x	*y*	*z*
Sn	3300(0)	5017(0)	5009(0)
Cr	2292(1)	3086(1)	3722(1)
S(1)	4287(1)	6634(1)	4574(1)
S(2)	4238(1)	4514(2)	6914(1)
O(1)	1272(4)	2437(5)	5188(4)
O(2)	556(3)	4744(5)	2243(4)
O(3)	3295(4)	3859(5)	2253(4)
O(4)	1330(4)	718(5)	2342(4)
O(5)	3884(3)	1134(5)	5078(4)
C(1)	1659(4)	2712(6)	4647(5)
C(2)	1225(4)	4156(6)	2831(5)
C(3)	2938(4)	3554(6)	2821(5)
C(4)	1700(4)	1628(6)	2855(5)
C(5)	3313(4)	1917(6)	4583(5)
N	2780(3)	6931(4)	5696(3)
C(11)	4433(5)	7666(6)	5731(6)
C(12)	3465(5)	8069(6)	5765(6)
C(21)	3943(5)	5975(8)	7512(5)
C(22)	2937(5)	6531(8)	6831(5)
C(6)	1706(4)	7323(6)	5020(5)
C(7)	1013(4)	6190(7)	5035(6)
C(8)	1555(5)	7553(7)	3822(5)
C(9)	1428(5)	8629(7)	5461(6)
H(1)	490(4)	710(6)	639(5)
H(2)	477(4)	841(6)	570(4)
H(3)	367(5)	852(7)	656(5)
H(4)	309(4)	848(6)	512(4)
H(5)	454(5)	669(7)	766(6)
H(6)	400(5)	565(8)	825(6)
H(7)	239(6)	577(8)	668(6)
H(8)	285(4)	727(6)	714(5)

TABLE 3

BOND LENGTHS (Å) WITH STANDARD DEVIATIONS

Cr–Sn	2.622(1)
S(1)–Sn	2.426(1)
S(2)–Sn	2.423(1)
N–Sn	2.400(4)
C(1)–Cr	1.899(6)
C(2)–Cr	1.883(6)
C(3)–Cr	1.907(6)
C(4)–Cr	1.853(6)
C(5)–Cr	1.893(6)
C(11)–S(1)	1.815(6)
C(21)–S(2)	1.816(7)
C(1)–O(1)	1.142(7)
C(2)–O(2)	1.149(7)
C(3)–O(3)	1.148(7)
C(4)–O(4)	1.140(7)
C(5)–O(5)	1.147(7)
C(12)–N	1.510(7)
C(22)–N	1.511(7)
C(6)–N	1.533(6)
C(12)–C(11)	1.523(8)
C(22)–C(21)	1.506(9)
C(7)–C(6)	1.544(8)
C(8)–C(6)	1.562(8)
C(9)–C(6)	1.566(8)
H(1)–C(11)	1.05(6)
H(2)–C(11)	0.91(6)
H(3)–C(12)	1.09(6)
H(4)–C(12)	0.92(5)
H(5)–C(21)	1.10(7)
H(6)–C(21)	1.02(7)
H(7)–C(22)	1.08(8)
H(8)–C(22)	0.89(6)

The structure of the complex is illustrated in Fig. 1, and the packing in the unit-cell in Fig. 2.

The atomic coordinates are given in Table 2, and the bond lengths and the bond angles in Tables 3 and 4, respectively. The coordination around the Cr atom is a nearly perfect octahedron, while that around the Sn atom is a distorded tetrahedron.

The tin–nitrogen bond length of 2.40 Å is 0.17 Å shorter than in the 1-methyl-5,5-dimethyldipychthiazastannolidine [5,6], reflecting a stronger Lewis-acceptor capacity of the tin(II) complex. In the (di-t-butylstannylene)pyridinopentacarbonylchromium the Sn–N bond is 0.11 Å shorter [7]. The tin–sulfur distances are in the expected range for a single bond [8,11,12]. The Sn–Cr bond length is nearly the same as in the $Bu^t_2SnCr(CO)_5 \cdot py$ [7] but significantly longer than in $[(Me_3Si)_2CH]_2SnCr(CO)_5$ [9]. This reflects a decreased d_π–p_π interaction in the two former compounds due to the higher electron density at the tin atoms. The tin atom in the title compound lies 0.50 Å above the plane defined by the atoms Cr, S(1) and S(2); in ref. 7 the tin atom deviates by 0.44 Å from the plane Cr,C,C; in ref. 9 no

TABLE 4

BOND ANGLES (°) WITH STANDARD DEVIATIONS

S(1)-Sn-Cr	124.8(0)	O(1)-C(1)-Cr	177.3(6)
S(2)-Sn-Cr	118.2(0)	O(2)-C(2)-Cr	175.8(5)
S(2)-Sn-S(1)	104.9(1)	O(3)-C(3)-Cr	177.4(5)
N-Sn-Cr	131.3(1)	O(4)-C(4)-Cr	178.2(6)
N-Sn-S(1)	83.6(1)	O(5)-C(5)-Cr	175.0(5)
N-Sn-S(2)	83.7(1)	C(12)-N-Sn	107.8(3)
C(1)-Cr-Sn	90.7(2)	C(22)-N-Sn	104.2(3)
C(2)-Cr-Sn	96.0(2)	C(22)-N-C(12)	109.0(5)
C(2)-Cr-C(1)	90.8(3)	C(6)-N-Sn	113.7(3)
C(3)-Cr-Sn	86.6(2)	C(6)-N-C(12)	111.0(4)
C(3)-Cr-C(1)	177.0(2)	C(6)-N-C(22)	110.9(4)
C(3)-Cr-C(2)	88.3(2)	C(12)-C(11)-S(1)	113.8(4)
C(4)-Cr-Sn	174.1(2)	C(11)-C(12)-N	115.3(5)
C(4)-Cr-C(1)	91.5(3)	C(22)-C(21)-S(2)	113.0(5)
C(4)-Cr-C(2)	89.4(2)	C(21)-C(22)-N	114.5(5)
C(4)-Cr-C(3)	91.3(2)	C(7)-C(6)-N	110.2(4)
C(5)-Cr-Sn	87.4(2)	C(8)-C(6)-N	108.7(4)
C(5)-Cr-C(1)	88.1(2)	C(8)-C(6)-C(7)	108.4(5)
C(5)-Cr-C(2)	176.5(2)	C(9)-C(6)-N	111.4(5)
C(5)-Cr-C(3)	93.0(2)	C(9)-C(6)-C(7)	108.8(5)
C(5)-Cr-C(4)	87.2(2)	C(9)-C(6)-C(8)	109.2(5)
C(11)-S(1)-Sn	92.1(2)		
C(21)-S(2)-Sn	99.7(2)		

deviation was observed. However, the other atoms attached to the tin can influence the nature of the tin–chromium bond, and therefore it would be better to be able to compare our data with these for the still unknown complexes such as $(RS)_2SnCr(CO)_5$ and $(RS)_2SnCr(CO)_5 \cdot py$.

Eight-membered organotin(IV) compounds of the type $R_2Sn(SCH_2CH_2)_2Y$ with $Y = O$, S and NMe generally exhibit chair-chair, boat-chair [5,10] or intermediate conformations [11,12]. In our complex there is a boat-boat conformation (Table 5), perhaps due to the shortening of the Sn–N bond length in comparison to $Me_2Sn(SCH_2CH_2)_2NMe$ [5]. A similar conformation was found in $Sn[(OCH_2CH_2)_2NCH_2CH_2OH]_2$ [13].

TABLE 5

TORSION ANGLES (°)

S(1)-Sn-S(2)-C(21)	+78.60
Sn-S(2)-C(21)-C(22)	+30.41
S(2)-C(21)-C(22)-N	−58.36
C(21)-C(22)-N-C(12)	−64.47
C(22)-N-C(12)-C(11)	+95.14
N-C(12)-C(11)-S(1)	+53.60
C(12)-C(11)-S(1)-Sn	−54.70
C(11)-S(1)-Sn-S(2)	−50.04

Experimental

All manipulations were carried out under dry argon. The solvents were dried by standard methods and freshly destilled before used. The NMR spectra were recorded on a spectrometer Bruker WP 200, and the IR spectra on a Beckmann IR 12 instrument using KBr discs.

Pentacarbonyl-5-t-butyl-5-aza-2,8-dithia-1-stannobicyclo[3.3.0^{1,5}]octanechromium-(0). A solution of 1.3 g (4.4 mmol) $Sn(SCH_2CH_2)_2NBu^t$, in 200 ml THF was added dropwise to a solution of 6.8 mmol $Cr(CO)_5 \cdot THF$ in 300 ml THF. The mixture was stirred for 3 h at room temperature and than evaporated under vacuum. The precipitate was filtered off and recrystallised from benzene (yields 1.4 g (64%), m.p. 190°C (dec.)). Found: C, 31.24; H, 3.95; N, 2.68; S, 12.96. $C_{13}H_{17}NS_2Sn$ calcd.: C, 31.09; H, 3.82; N, 2.75; S, 12.76%.

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