# Synthesis of Tin (IV) Complexes of Coordination Number Six

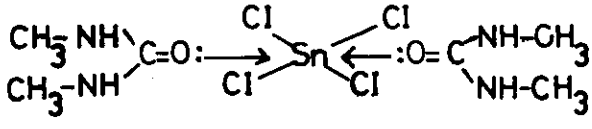
RAJA HUSSEIN ABU-SAMN
*Chemical Engineering Department, Faculty of Engineering, King Saud University, Riyadh, Saudi Arabia*

(Received 11th January, 1982)

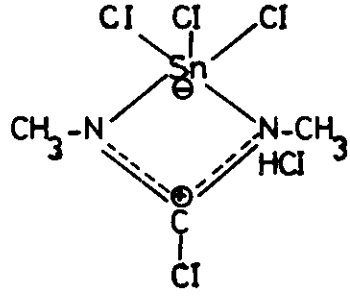
**Summary:** A 1:2 adduct of tin tetrachloride with substituted urea was reported. By applying different techniques and conditions various coordination complexes of tin (IV) have been obtained. A series of tin (IV) complexes were synthesized and identified by the reaction of $SnCl_4$ or the disubstituted tin (IV) tetrachloride, $R_2SnCl_2$, with 1,3-disubstituted urea or thiourea. In all these complexes, the coordination number (4) of tin is thus increased to (6). The complexes were characterized by elemental analysis as well as by physical methods such as i.r., $^1$H-n.m.r. and mass spectroscopy.

## Introduction

Aggarwal and Singh have reported the 1:2 adduct of $SnCl_4$ with 1,3-dimethyl urea [1]. By mixing the two reactants in $CHCl_3$ at low temperature they obtained a viscous liquid which upon cooling gave a white precipitate. Through recrystallization from nitromethane they obtained the 1:2 adduct



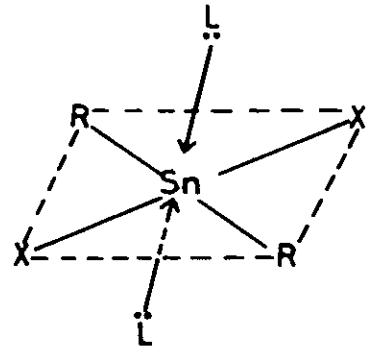
(m.p = 195°C). The reaction has been repeated in $CCl_4$ under reflux and under vacuum to afford a four membered heterocyclic compound, in which the carbonyl group of the disubstituted urea undergoes chlorination [2].



Upon variation of the reaction conditions such as the reactant's mole ratio, temperature, pressure, different products [3] have been obtained. The above heterocyclic compound was prepared by the reaction of 1,3-dimethyl carbomide chloride with $SnCl_4$ (tin tetrachloride) [4].

However by using the substituted organo halides of $SnCl_4$, different adducts have been prepared by reaction with DMSO=dimethyl sulfoxide [5], pyridine [6], 1,10 phenanthroline [7], 2,2-bipyridyl [8] and 8-hydroxyquinoline [9]. The new synthesized complexes of diorgano--dihalides of tin–tetrachloride $R_2SnX_2$. 2L., with different ligands (L), have the common formulae $R_2SnX_2.L_2$. or $R_2SnX_2$. 2L.

In all these complexes, the ligand is attached to the central atom of tin through the lone pair of electrons, forming a coordination bond.



I: R=R' =$CH_3$, L = 1,3-dimethyl urea

II: R=R' =$C_6H_5$, L= 1,3-dimethyl urea

III: R=R' =X=Cl, L= 1,3-diphenyl urea

IV: R=R' =$C_6H_5$, L= 1,3-dimethyl thiourea

V: V=R' =$CH_3$, L - 1,3-dimethyl thiourea

The ligands (L) generally considered as Lewis base or as electron donors were disubstituted urea or thiourea such as 1,3-dimethyl urea, 1,3-diphenyl urea and 1,3-dimethyl thiourea whereas tin atom of either $SnCl_4$ or $R_2SnCl_2$ plays the role of Lewis acid or the electron acceptor. In the formed complexes, the coordination number (4) of tin is thus increased to (6) in the octahedral configuration.

In all the complexes prepared and discussed in this paper the ligands are monodentate, in which the Sn atom is bonded either to the oxygen atom of the disubstituted urea molecule or to the sulfur atom of the thiourea molecule [10].

## Experimental

*1- Preparation of dichloro-dimethyl-bis(1-3-dimethyl urea) tin(IV), [( $(CH_3)_2Sn(CH_3NHC=ONHCH_3)_2Cl_2$)] [1]:–* 2.20 g (0.01 M) of dimethyl tin dichloride $(CH_3)_2SnCl_2$ and 1.76 g (0.02 M) of 1,3-dimethyl urea were heated in 50 ml absolute benzene solution until boiling under reflux. The reaction suspension becomes turbid at the beginning. At 50°C it becomes a clear solution. After 20-30 minutes of reflux the reaction is stopped and upon cooling, glassy colorless crystals are obtained and dried.

Yield = 3.8 g = 96% m.p. = 63-65°C from benzene/ether Elemental analysis of (I) $C_8H_{22}N_4Cl_2O_2Sn$ (M. Wt. = 395.910): calc: C 24.26%, H 5.60%, N 14.15%, Cl 17.91%, Sn 29.97%, O 8.10%;
found: C24.46%, H 5.65%, N 13.80%, Cl 17.98% Sn 29.0%.

*2. Preparation of dichloro-diphenyl-bis (1,3-dimethyl urea tin) (IV) [$(C_6H_5)_2Sn(CH_3–NH-CO-NHCH_3)_2Cl_2$] (II):–* 3.44 g (0.01 M) of diphenyl tin dichloride $(C_6H_5)_2SnCl_2$ were refluxed with 1.76 g (0.02 M) of 1,3-dimethyl urea in 50 ml of either absolute $CCl_4$ or benzene. After 10 m a white precipitate separates. After 4 h the reaction is finished and the product is filtered off, washed withe benzene and petroleum ether and dried. Yield: 4.85 g=93%, m.p. = 128/130°C from benzene, 128°C from 1,2-dichloro ethane, and 130/131°C from methylene chloride. Elemental analysis of (II) $C_{18}H_{26}N_4Cl_2O_2Sn$ (M. Wt. = 520.054),
calc. C 41.57%, H 5.04%, N 10.78%, Cl 13.64%, Sn 22.83%, O 6.15%; found: C 41.47%, H 5.00%, N 10.34%, Cl 13.34%, Sn 22.36%.

*3. Preparation of tetra-chloro-bis (1,3-diphenyl urea) tin (IV) [$Sn(C_6H_5NHC=ONHC_6H_5)_2Cl_4$] (III)*
A 0.5 M (10.6 g) of 1,3-diphenyl urea $C_6H_5NCHO-NHC_6H_5$ was suspended in hot absolute benzene in a 100 ml two necked round bottom flask provided with a Liebig's condenser and a dropping funnel. A 0.5 Mole of water free tin tetrachloride $SnCl_4$ (13.0 g) was added dropwise to the boiling suspension of the 1,3-diphenyl urea under magnetic stirring and reflux. As soon as $SnCl_4$ is dropped, the thick white suspension of 1,3-diphenyl urea is dissolved and gradually becomes a clear solution and changes to brown. The reaction mixture was cooled and filtered under water pump vacuum after completion of the reaction ca. 2-3 h. The end product is washed then with petroleum ether (60-70°C) and dried under vacuum. m.p. = 45-50°C, Yield=50% (1:2) ratio and 75% (1:1) ratio. Elemental analysis of (III): $C_{26}H_{24}Cl_4N_4O_2Sn$ (M. Wt. = 685.004):
calc. C 45.59%, H 3.53%, Cl 20.70%, Sn 17.33 %, N 8.17%, O 4.67%; found C 45.61%, H 3.72%, Cl 20.90%, Sn 16.5%, N 6.54.

*4. Preparation of dichloro-diphenyl-bis (1,3-dimethyl thiourea) tin (IV) [$(C_6H_5)_2Sn(CH_3NHC=SNHCH_3)2Cl_2$] (IV)*

To a cold or a hot suspension of 2.08 g (0.02 M) of 1,3-dimethyl thiourea, 3.43 g (0.01 M) of diphenyl tin dichloride $(C_6H_5)_2SnCo_2$ are added under reflux. At the beginning a yellowish gel turbid substance is formed, then a white substance is precipitated. After 60 min the reaction mixture is filtered and washed with petroleum ether and dried in vacuum. The yield is 5.4 g = 98.2%, m.p. = 112/115°C (crude product), 122/125°C after twice recrystallization from 1,2-dichloroethane. Elemental analysis of (IV), $C_{18}H_{26}N_4Cl_2SnS_2$ (M. Wt.=552.186):–
calc. C 39.16%, H 4.75%, N 10.14%, Cl 12.85%, S 11.61%, Sn 21.5%; found C 39.04%, H 4.99%, N 9.84%, Cl 12.87%, Sl 1.51%, Sn 20.9%.

*5. Preparation of dichloro-dimethyl-bis (1,3-dimethyl thiourea)tin (IV), [$(CH_3)2Sn(CH_3NHC=SNHCH_3)_2Cl_2$] (V):–*

To an absolute suspension of 1.04 g (0.01 M) of 1,3-dimethyl thiourea either on cold or hot under

reflux and stirring, 1.10 g (0.005 M) dimethyl tin dichloride $(Ch_3)_2SnCl_2$ are added. A white precipitate is formed which upon recrystallization from 1,2-dichloroethane gives white needles. Yield= 2.1 g=98.1%, m.p.=105-108°C (crude product), =115-118°C (after 3 recrystallization from 1,2-dichloroethane). Elemental analysis of (V) $C_8H_{22}N_4Cl_2S_2Sn$ (M. Wt.= 428.042); calc. C 22.45%, H 5.18% N 13.09%, Cl 16;57%, S 14.98% Sn 27.73%; found C 22.45%, H 5.09%, N 12.95% Cl 16.60%, S 15.26%, Sn 26.6%.

**Results and Discussion**

Complex (I) is colourless crystalline and sensitive to moisture. It is soluble in benzene and all chlorinated hydrocarbon solvents, but it is insoluble in ether or petroleum ether.

Complex (II) like (I) is colourless crystalline, but is not sensitive to moisture. It dissolves in most of normally used organic solvents except carbon tetrachloride. The molecular weight determination of (I) (395. 910) and (II) (520.054) by different methods i.e. cryoscopic in benzene or acetone, osmometric in acetone or 1,2-dichloroethane and over vapor pressure in $CHCl_3$ gave always about half the value of the theoretical (200) for (I) and 250 for (II).

The ligands i.e. 1,3-dimethyl urea molecule in (I) and (II) are attached through their carbonyl groups to the tin atom. This is proved from the magnetic equivalence of their methyl groups in $^1$H-n.m.r. spectra as well as from their i.r. spectra which show the absorption bands at 1650 $cm^{-1}$ (I) and 1640 $cm^{-1}$ (II), which is characteristic for similar Co-donor complexes [11-12].

The important bands in i.r. spectra of (I) and (II) are summarized in Table 1:

The $^1$H.n.m.r. spectrum of (I) in $D_6$-acetone against TMS (tetramethylsilane) as an internal standard shows a signal at $\delta$ = 1.15 ppm in the region of Sn-$CH_3$ with 2 satellites ($J_{^{119}Sn\text{-}CH_3}$ = 58 c.p.s.). which is in agreement with the literature [13,14].

The $^1$H.n.m.r. spectra of (I) and (II) in $D_6$-acetone shows the following signals corresponding to protons: (I) at $\delta$ = 1.15 ppm, 6H of $Sn(CH_3)2$; 2,73 ppm, 12H of 4(-N-$CH_3$) and four protons of the 4(-NH) at 5.95 ppm. (II) at $\delta$ = 2.62 ppm, 12 H of 4(-N-$CH_3$); 5.35 ppm, 4H of 4(-NH) and 10 H at 7.65 ppm of $Sn(C_6H_5)_2$.

Table 1 The assignment of the i.r. spectra of Complexes (I) & (II) in KBr ($cm^{-1}$)

| Complex (I) | Complex (II) | Assignment |
|---|---|---|
| 3390 (s) | 3325 (s) | $\nu$NH |
| – | 3065, 3045 (s) | $\nu$CH-aromatic |
| 1650, 1605 (s) | 1640, 1615 (s) | $\nu$C=O (amide I) |
| – | 735, 698 (vs) | $\nu$ mono substituted benzene |
| 564 (m) | 567 (s) | $\nu$Sn-C asym. |
| 527 (sh) | 513 (s) | $\nu$Sn-C sym. |
| 523 (m) | 500 (m) | $\nu$Sn-O |

The mass spectra of (I) and (II) gave nearly the most possible fragments, however the molecular ions do not appear [15].

The exact arrangement of ligands is still open [10,15], although the trans-configuration of 1,3-dimethyl urea molecule and the cis-chlorine atoms is suggested [16].

Complex (III) is a crystalline, colourless and hygroscopic substance which dissolves in most of the organic solvents. However when complex (III) is dissolved either in acetone or in hot ethyl alcohol, the 1,3-diphenyl urea is formed in fine crystalline needles. The mass spectrum and fragments of (III) support its structure: m/e= 260 = $SnCl_4$ 225=$SnCl_3$, 212=$C_6H_5NH$-C-$NHC_6H_5$, 190=SnCl, 119=$C_6H_5$-NCO, 93=$C_6H_5NH_2$, 91=$C_6H_5N$, 78=$C_6H_6$, 77=$C_6H_5$; the most important bands in i.r. absorption spectroscopy of complex (III) which help in its characterization are:– (in $cm^{-1}$): 3310 s ($\nu$NH), 3040 w ($\nu$CH-aromatic), 1650 sh ($^{\delta}$ NH), 1550 s ($^{\nu}$ C=O), 1490 s. 1445 , ($^{\nu}$N=C=O; amide I+III), 1400 m, 1360m ($\delta$ CH-aromatic), 750 vs, 695s (mono substituted benzene) 540 m ($\nu$Sn-O); the $^1$H.n.m.r. spectrum of (III) in $d_6$-benzene gave signals $\delta$ = 7.15 ppm (phenyl protons) and $\delta$ = 7.78 ppm for the (NH protons) in a ratio of 5:1 [17].

Also the $^1$H.n.m.r. spectrum of (III) in $D_6$-acetone shows the multiplet of phenyl groups at $\delta$5.7 ppm and the NH protons at $\delta$=6.3 ppm in a ratio of ca. 5:1 [17].

In the case of 1,3-dimethyl thioruea as a ligand, complexes (IV) and (V) were formed, with diorgano tin dihalides, in which the thiourea molecules are attached to the central atom of tin through sulfur

atoms forming Sn-S band. Since no X-ray structure had been performed for (IV) and (V), it is difficult to decide whether the thiourea molecules are cis or trans to each other [18,19]. Complex (IV) is colorless crytalline and is not sensitive to air moisture. The crude product is slightly yellow. Complex (IV) dissolves in benzene, nitrobenzene, nitromethane and 1,2-dichloroethane but does not dissolve in cyclohexane, ether, petroleum ether, carbon tetrachloride or chloroform. Complex (V) is obtained as needles, insoluble in benzene, ether, petroleum ether, carbon tetrachloride, methylene chloride and cyclohexane; but soluble in chloroform and recrystallizes from hot 1,2-dichloroethane. Table-2 gives the assignment of i.r. spectra for (IV) and (V) compared to the ligand 1,3-dimethyl thiourea [20].

From the i.r. spectra of (IV) & (V) and from Table 2, we notice that in the region between 800-400 $cm^{-1}$, there are no bands at 500 $cm^{-1}$, which indicates the absence of the N-Sn-N band [21].

A positive shift in the frequency of the NH stretching vibration and a negative shift in the frequency of the C=S band in both complexes (IV) and (V) has been observed as compared to the thiourea molecule which indicates that bonding is taking place between Sn-S and not through Sn-N.

The $^1$H-n.m.r. spectrum of complex (V) in $CDCl_3$ shows one signal at $\delta$ = 1.28 ppm in the area

Table 2 The assignment of the i.r.spectra in KBr($cm^{-1}$) of complexes (IV) and (V) compared to the Ligand 1,3-dimethyl thiourea (1,3-DMTU).

| 1,3-DMTU | Complex (IV) | Complex (V) | Assignment |
|---|---|---|---|
| 3220 s.br. | 3255 s | 3260 s | $\nu$NH |
| 3025 w. | 3048 w | 3048 | $\nu CH_3$ asym. and sym. |
| 2940 w.. | 2945 w | 2925 | |
| | 2832 w | 2848 | |
| – | 2050 - 1800 w | – | Benzene print |
| 1560 s | 1590 s | 1535 s | $\delta$NH |
| | 1570 sh | | |
| 1520 m | 1533 m | 1530 s | $\nu$N-C-N |
| | 1475 m | | |
| 1448 m | 1435 m | 1435 m | $\nu$N-C=S |
| | 1425 sh | | |
| | 1420 m | | |
| | 1369 m | 1370 m | $\delta$ $CH_3$ sym. |
| 1350 s | 1295 s | 1295 s | $\nu$(C=S) + $\delta$(NCS) |
| | 1280 sh | | |
| – | 1058 w | – | $\delta$CH-aromatic |
| | | 1200 – 1100 (4m bands) | |
| 1035 s | 1030 s | 1030 s | $\nu$(C-N) + $\delta$(NCN) |
| 1010 m | 1010 m | 1010 m | Ligand vibration |
| – | 985 w, 840 w | – | mono substituted benzene |
| 720 m | 695 s | 678 m | $\nu$(C-S) + $\delta$(NCS) |
| 642 m | 642 m | 626 s | |
| | 590 s. br. | 573 m br. | Ligand vibration |
| | 543 m | 547 s | $\nu$Sn-C asym. |

Abbreviations: s=strong, m=medium, w=weak, br=broad, sh=shoulder, vs=very strong

of Sn-$CH_3$ with two satellites for which the coupling constant $J_{^{119}Sn\text{-}CH_3}$ = 58 c.p.s. [13], and a signal (singlet) at $\delta$ = 3.04 ppm for the $CH_3$ protons of the 1,3-dimethyl thiourea and a broad signal of the NH protons between 5.5 – 6.5 ppm in a ratio of 3:6:2 of Sn-$CH_3$ with two satellites for which the coupling constant $J_{^{119}Sn\text{-}CH_3}$ = 58 c.p.s. [13], and a signal (singlet) at $\delta$ = 3.04 ppm for the $CH_3$ protons of the 1,3-dimethyl thiourea and a broad signal of the NH protons between 5.5 – 6.5 ppm in a ratio of 3:6:2 respectively. On the other hand the ratio of protons from $^1$H.n.m.r. of complex (IV), phenyl:NH:$CH_3$ is 5:2:6. The mass spectra of (IV) and (V) show the important fragments: (IV): 338=$(C_6H_5)_2SnCl_2S$=C, 344=$(C_6H_5)_2SnCl_2$, 309=$(C_6H_5)_2SnCl$, 267=$C_6H_5SnCl_2$, 232=$C_6H_5SnCl$, 197=$C_6H_5Sn$, 154=$(C_6H_5)_2$, 120=Sn, 104=$(CH_3NH)_2C$=S, 77=$C_6H_5$, 74=$CH_3$-NH-C=S, 30=$CH_3$-NH.

(V): 249=$CH_3SnCl_2C$=S, 220=$(CH_3)_2SnCl_2$, 205=$CH_3SnCl_2$, 185=$(CH_3)_2SnCl$, 155=SnCl, 135=SnCl, 135=$SnCH_3$, 120=Sn, 104=$(CH_3-NH)_2$ C=S, 74=$CH_3NHC$=S.

**Acknowledgement**

The author is grateful to DAAD (German Academic Exchange Service), Bonn-Bad Godesberg, Federal Republic of Germany. The valuable discussions of Professor R. Schmidt of Constance University, FRG and Professor L. M. Venanzi of Technical University of Zurich, Switzerland are appreciated. The author wishes to express his deep gratitude to Professor M. Afzal for his encouragement and reading the manuscript.

**References**

1. R. C. Aggarwal and P.P. Singh, *J. Inorg. Nucl. Chem.*, **26**, 218 (1965).
2. R. H. Abu-Samn, M. Sc. Thesis, Heidelberg (1970).
3. R. H. Abu-Samn Sixth International Congress of Heterocyclic Chemistry, Tehran, Iran, 9-13 July 1977.
4. R. H. Abu-Samn, Seventh International Congress of Heterocyclic Chemistry, Tampa, Tampa, Florida, USA, 12,17 August 1979.
5. R. S. Randall, R. W. Wedd and J. R. Sams *J. Organomet. Chem.*, **30**, 19(1971).
6. I. R. Beattie *Quart. Rev.*, **17**, 382 (1963).
7. T. Tanaka, M. Komura Y, Kawasaki and R. Okawara, *J. Organomet. Chem.*, *1*,484 (1964).
8. D. L. Alleston and A. G. Davies, *J. Chem. Soc. (London)*, 2050, (1962).
9. D. Blake, G. E. Caates and J.M. Tate, *J. Chem. Soc. (London)*, 756 (1961).
10. R.H. Abu-Samn, Ph.D. Dissertation, Heidelberg (1972).
11. W. Gerard, M.R. Lappert, H. Pyszora and J.W. Wallis, *J. Chem, Soc. (London)*, 2142 (1960).
12. E.W. Randall, C.M.S. Voder and Zuckermannj. *J. Inorg. Chem.*, **5**,2240 (1960).
13. V. K. G. Das and W. Kitching, *J. Organomet. Chem.*, **10**,59 (1967).
14. Fluck E, "Die Kernmagnetische Resonanz and ihre Anwendung in der Anorganischen Chemie, Springer Verlag, Berlin, Gottingen, Heidelberg, p.235 (1963).
15. R.H. Abu-Samn and H.P. Latscha, *Chemiker-Ztg.*, **96**, 222 (1972).
16. B. Kruss, Ph.D. Dissertation, Heidelberg (1972).
17. R.H., Abu-Samn, *Libyan J. Sci.*, **8b**, 85 (1978).
18. E.A. Blom, B.R. Penfold and W.T. Robinson *J. Chem. Soc.*, (A), 913 (1969).
19. N.W. Isaacs and C.H.L. Kennard, *J. Chem. Soc., (A).*, 1257 **(1970)**.
20. R.H. Abu-Samn and H.P. Latscha; *Egypt J. Chem.*; **16**, 373 (1973).
21. U. Wannagat, E. Bougusch and R. Braun *J. Organomet. Chem.*, **19**,367 (1969).