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Synthesis of Tetrachloro [*N*,*N*′-Dimethyl Oxamide]Tin (IV)

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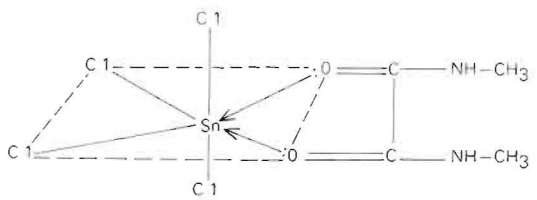
ABSTRACT. By the reaction of *N*,*N*′-dimethyl oxamide with water-free tin tetrachloride in the molar ratio (1:1), in hot pure 1,2-dichloroethane as a solvent, a white powdery complex is obtained, where the bidentate ligand (*N*,*N*′-dimethyl oxamide) is bound to the central atom (Sn) of the prepared octahedral complex through the oxygen donors.

The synthesized complex is of the type $SnCl_4$ LL, in which the coordination number of tin (4) in $SnCl_4$ is increased to (6) in the complex.

The paper describes the preparation and properties of the complex and also includes its IR, ^{1}H-NMR spectra, and the fragments of its mass spectrum.

Previous papers have reported the synthesis of hetrocyclic (four-membered) tin compounds with urea derivatives (Abu-Samn 1977) and with 1,3-dimethyl carbamide chloride (Abu-Samn 1979a). Also the synthesis of complexes of the type R_2SnCl_2. 2L was given, where L is a monodental ligand such as 1, 3-dimethyl urea (Abu-Samn and Latscha 1972) and 1,3-dimethyl thio urea (Abu-Samn 1973) using the dialkyl and diaryl tin dihalides. In these complexes, the ligands are coordinated to the tin atom through their oxygen or sulphur atoms as electron donors or Lewis bases in 1:2 ratio, where the coordination number of tin (4) in R_2SnCl_2 is increased to (6) by complexing two molecules of the monodentate ligands in the octahedral complex.



(I) (M.w.t.=376.652)

By studying the reaction of amides, urea and thiourea derivatives with the reactive tin tetrachloride, mostly complexes of the type $SnCl_4.L_2$ were obtained (Abu-Samn 1973, Abu-Samn 1979b). In this paper, the author presents the synthesis of a new complex of the type $SnCl_4.LL$, where LL is a bidental ligand: *N*,*N*′-dimethyl oxamide, which is bound to the tin atom through the oxygen donors of both carbonyl groups as in the given structure (I).

Complexes of the same type $SnCl_4.LL$ have been prepared and characterized as tetrachloro oxamide tin IV (Jain and Rivest 1969) and tetrachloro fumaric acid tin IV (Yeats *et al.* 1970).

By the reaction of tin (IV) tetrachloride (water-free) with *N*,*N*′-dimethyl oxamide in molar ratio (1:1) in hot pure 1,2-dichloroethane, a white powdery substance was formed, which after purifying by sublimitation and elemental analysis indicates the formula $C_4H_8N_2Cl_4O_2Sn$, which is in agreement with the above shown structure (I).

Experimental

In a 250 ml two neck round bottom flask equipped with Liebig condenser and a dropping funnel, a 5.8 g (0.05 *M*) *N*,*N*′-dimethyl oxamide is dissolved with stirring in a hot solution of pure 1,2-dichloroethane. To this solution, we add dropwise 13.0 g (0.05 *M*) water-free tin tetrachloride in molar ratio (1:1). As soon as $SnCl_4$ is added a white precipitate is formed. After all the $SnCl_4$ is added, stirring should continue further for 5-10 min. The reaction temperature is maintained at 80-90°C. The reaction mixture is then cooled and filtered. The product is washed with benzene and petroleum ether and dried in vacuum.

During the reaction no hydrogen chloride evolves. The yield is 18.5 g = 98.4%. The product does not melt below 360°C. The sublimate has mp 275/278°C in closed capillary tube. Elemental analysis of tetrachloro [*N*,*N*′-dimethyl oxamide]tin (IV) $C_4H_8N_2Cl_4O_2Sn$ (M.Wt. = 376.652):

	C%	H%	N%	Cl%	Sn%	O%
calc.	12.76	2.13	7.43	37.66	31.52	8.50
found	13.04	2.29	7.43	37.52	30.90	–

Results and Discussions

Figures 1-3 give the IR of complex I and its ^{1}HNMR Spectra. The properties of the prepared complex and the following discussion are given below. The major fragments of the mass spectrum of Complex I are also given.

Properties of Complex (I)

The complex is a white powder and is not hygroscopic. It does not dissolve in $CHCl_3$, CCl_4, 1,2-dichloroethane, methylene chloride, benzene and petroleum ether. It is relatively soluble in cold acetone, dimethyl sulfoxide, acetonitrile, and ethyl acetate. The substance is sublimable. No melting point for the product could be detected below 300°C. It was purified by sublimation and the pure product has a mp of 275/278°C in closed mp tube.

Identification of $C_4H_8N_2Cl_4O_2Sn$ and Discussion

Complex (I) is a 1:1 adduct, in which the tin atom functions as an acceptor or Lewis acid and the *N*,*N*'-dimethyl oxamide as a bidentate donor ligand or Lewis base.

The *N*,*N*'-dimethyl oxamide molecule is bound to the tin atom in the octahedral complex (I) through the oxygen atoms of the two carbonyl groups.

The stereochemistry is ambiguous in contrast to the previously synthesized complexes of the type R_2SnCl_2, 2L or $SnCl_4$.2L, as the two carbonyl groups of the bidentate ligand are bonded to the same tin atom in a cis-configuration, so that a C_{2v}-symmetry is applicable for the complex (Jain and Rivest 1969).

In the IR spectrum of complex (I) in KBr, we recognize two bands which are characteristics for Sn-O at 510 cm^{-1} and 540 cm^{-1} (m). Also we see in the Nujol IR spectrum of the complex four characteristic bands of the Sn-Cl at 372 cm^{-} (m), 345 cm^{-1} (m), 330 cm^{-1} (vs) and at 280 cm^{-1} (w). The number of bands (2) for SnO and (4) for Sn-Cl is in agreement with the calculated number of bands for the molecule (I) (Jain and Rivest 1969). (m = medium, w = week, s = strong, vs =

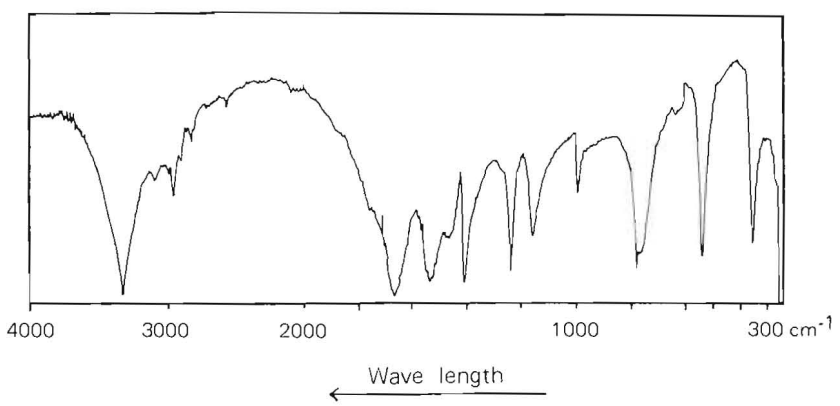


Fig. 1. IR spectrum of complex (I) $SnCl_4$ $(CONHCH_3)_2$ in KBr (4000-250 cm^{-1})

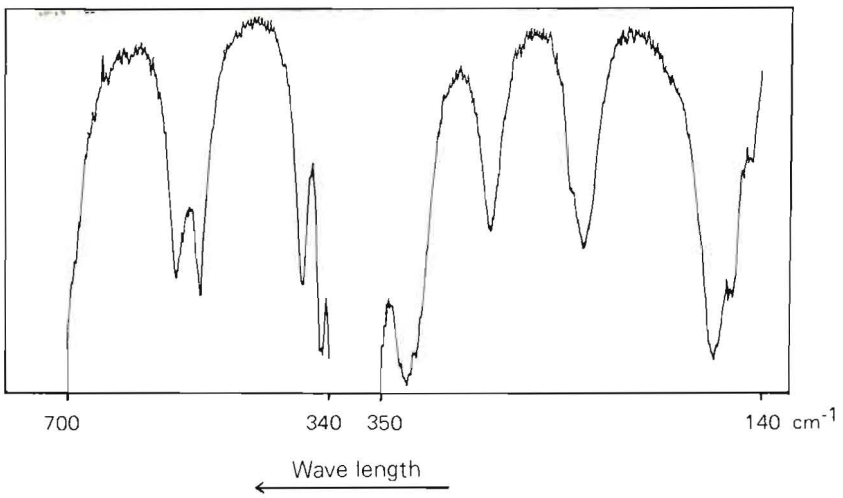


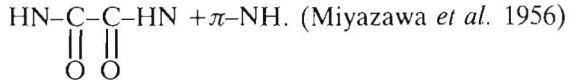
Fig. 2. IR spectrum of complex (I) in Nujol/polythylene (140-350 cm^{-1})

very strong). No band at 500 cm^{-1} is observed in IR spectra, which supports the absence of $Sn(N)_2$ vibration (Abu-Samn and Latscha 1973).

In addition, the following characteristic NH-vibrations are observed in the IR spectra:

1650 cm^{-1}	(vs)	Amide I	$\nu_C = O$
1572 cm^{-1}	(s)	Amide II	$\nu_C - N$
1275 cm^{-1}	(m)	Amide II	$\delta_N - H$

700, 780 and 790 cm^{-1} skeletal deformation vibration, *i.e.*



(Miyazawa *et al.* 1956)

In the ^{1}H-NMR spectrum of complex (I) in d_6-acetone there is at δ = 3.15 ppm a doublet for the methyl protons equivalent to 5.95 H, also at δ = 7.17 – 7.52 ppm(m), we recognize the NH-protons equiv. to 2.05 H. Thus, the ratio of the NH protons to the $-CH_3$ protons is 1:3.

The following fragments are seen from the M.S, of the complex (I).

m/e	fragment assignment
116	$O=C-NH-CH_3$ | $O=C-NH-CH_3$
260	$SnCl_4$
225	$SnCl_3$
190	$SnCl_2$
155	SnCl

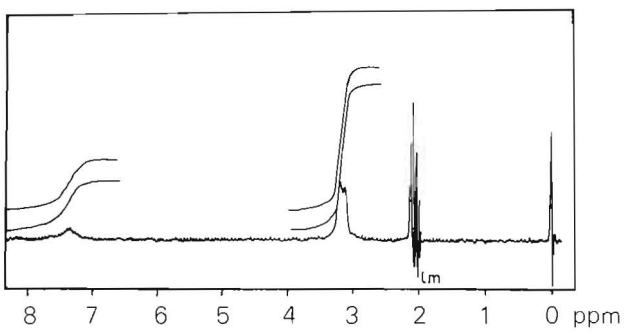


Fig. 3. ^{1}H-NMR spectrum of $C_4H_8N_2Cl_4O_2Sn$ in D_6-Acetone.

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بتفاعل ن، نَ - ثنائي مثيل الأوكساميد مع رابع كلوريد القصدير الخالي من الماء بنسبة جزيئية (١ : ١) فى ١، ٢ - ثنائي كلور الإيثان النقي الساخن كمذيب، أمكن الحصول على متراكب مسحوق أبيض حيث يرتبط جزىء المادة الثنائية الاشتباك (ن، نَ - ثنائي مثيل الأوكساميد) مع ذرة القصدير المركزية للمتراكب السداسي بواسطة ذرات الأكسجين المعطية.

إن المتراكب المحضر هو من النوع $SnCl_4.LL$ حيث إن رقم الارتباط (٤) للقصدير فى رابع كلوريد القصدير قد ازداد إلى (٦) فى المتراكب.

يصف البحث طريقة تحضير وخواص المتراكب الجديد، كما أنه يتضمن أشعة الطيف تحت الحمراء والرنين المغناطيسي البروتوني للمتراكب وكذلك أجزاء شعاع الكتل له.