

## Complexes of Sn(IV) & Ge(IV) Halides with Pyrimidines

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The preparation and characterization of Sn(IV) halides and Ge(IV) chloride complexes of pyrimidine and some of its derivatives have been described. The far infrared spectra of 1:1 and 1:2 complexes indicate a *trans*-octahedral geometry involving bidentate or unidentate ligands. A polymeric structure is proposed for the 1:1 complexes. The molar conductances of pyrimidine complexes in nitromethane indicate them to be covalent in nature.

COMPLEXES of Co(II) and Ni(II) with biologically important pyrimidine (1,3-diazine) bases have recently been reported<sup>1</sup>. To our knowledge there is no report on the complexes of Sn(IV) and Ge(IV) halides with pyrimidine or substituted pyrimidines. It was, therefore, of interest to prepare and study such complexes.

### Materials and Methods

2,4,6-Triaminopyrimidine (apy); 4-pyrimidinol (pyl); 4,6-diamino-2-mercaptopyrimidine (mpy) (all Fluka reagents) and 4-amino-1,3-dimethyl-2,6-dioxypyrimidine (opy) (Koch Light) were recrystallized from ethanol. Pyrimidine (pym) and GeCl<sub>4</sub> (both Koch Light reagents) were used as such. Sn(IV) halides were prepared according to standard methods<sup>3</sup>. All manipulations were done in a dry box.

Infrared spectra in 4000-650 cm<sup>-1</sup> region were recorded in KBr on a Perkin-Elmer spectrophotometer model 521 and in 650-200 cm<sup>-1</sup> region in nujol on a Beckman IR-12. Conductivity measurements were made on a Systronix type 301-1 bridge.

*Complexes of pyrimidine* — Pyrimidine complexes were prepared by mixing chloroform solutions of the ligand and the metal halides in 1:2 ratio. In each case a precipitate appeared immediately which was filtered, washed with chloroform and dried in vacuum desiccator. Sn(IV) chloride and bromide complexes were recrystallized from ethanol.

*Complexes of substituted pyrimidines* — Sn(IV) halide complexes were prepared by mixing equimolar alcoholic solutions of the metal halides and the ligand. 2,4,6-Triaminopyrimidine yielded needle-shaped crystals immediately but with other ligands it was necessary to heat the reactants for 1 hr and to leave the mixture for a few days. 4,6-Diamino-2-mercaptopyrimidine and 1,3-dimethyl-2,6-dioxypyrimidine yielded needle-shaped and granular crystalline products respectively. In the preparation of 4-pyrimidinol complexes of SnCl<sub>4</sub> and SnBr<sub>4</sub>, the yellow viscous mass obtained in each case after a week was heated to yield a solid product which was washed with benzene and recrystallized from ethanol to yield granular crystalline products. Excepting the 4-pyrimidinol complex of GeCl<sub>4</sub> which was obtained immediately after mixing their equimolar

solutions, the GeCl<sub>4</sub> complexes of all other ligands were obtained after keeping the equimolar solutions of the reactants in dry alcohol-chloroform mixture for a week.

### Results and Discussion

The analytical data which agree with the proposed stoichiometries are presented in Table 1. Only pym complexes are soluble in nitromethane and the molar conductances of their 10<sup>-3</sup>M solution [SnCl<sub>4</sub>(pym)<sub>2</sub>, 31.86; SnBr<sub>4</sub>(pym)<sub>2</sub>, 34.57; SnI<sub>4</sub>(pym)<sub>2</sub>, 38.01 and GeCl<sub>4</sub>(pym)<sub>2</sub>, 32.96 ohm<sup>-1</sup> cm<sup>2</sup> mole<sup>-1</sup>] indicate them to be covalent in nature<sup>3</sup>. Other complexes are not soluble in usual organic solvents.

*Infrared data\* in 4000-650 cm<sup>-1</sup> region: Pyrimidine and 2,4,6-triaminopyrimidine complexes* — In pym complexes the ring stretching vibrations appear in the higher frequency region (1638-1408) as compared to those of the free ligand at 1570, 1467 and 1402. This suggests coordination through the ring nitrogen atom<sup>4-6</sup>. The apy complexes do not show any significant decrease in ν(N-H) vibrations (3378, 3268, 3058), however, the ring stretching vibrations (1634-1427 cm<sup>-1</sup>) on complexation show a positive shift indicating coordination through the ring nitrogen atom.

*4-Pyrimidinol complexes* — 4-Pyrimidinol (4-hydroxypyrimidine) is capable of existing in keto-enol form. Infrared studies<sup>7-12</sup> in solid state as well as in different solvents show that it occurs predominantly in the keto form. In chloroform solution it mainly assumes<sup>11</sup> the *ortho*-quinonoid amide form, the amount of *para*-quinonoid-isomer and the enol form being undetectable. Its complexes do not show any significant decrease in νN-H (3175, 3115) or an increase in ring stretching (1597-1416) ruling out coordination through nitrogen atoms. However, the νC=O at 1681 shifts by 60, 50 and 39 cm<sup>-1</sup> for SnCl<sub>4</sub>, SnBr<sub>4</sub> and GeCl<sub>4</sub> complexes, respectively, indicating coordination through the carbonyl group.

*4,6-Diamino-2-mercaptopyrimidine complexes* — The presence of an intense band at 1200 attributable to the νC=S and the absence of S-H band in the 2550-2600 region<sup>13,14</sup> in the free ligand suggest its existence in the thioamide form rather than in

\*IR ν<sub>max</sub> in cm<sup>-1</sup>.

TABLE 1 — CHARACTERIZATION DATA OF THE COMPLEXES

Complexes	Colour	m.p. (°C)	Calc. (%) (Found)				
			C	H	N	X	M
SnCl <sub>4</sub> (pym) <sub>2</sub>	White	262(d)	22.85 (22.46)	1.91 (1.95)	13.32 (12.98)	33.70 (33.81)	28.21 (27.25)
SnBr <sub>4</sub> (pym) <sub>2</sub>	Light yellow	243(d)	16.05 (16.66)	1.34 (1.38)	9.36 (9.81)	53.39 (53.01)	19.82 (20.21)
SnI <sub>4</sub> (pym) <sub>2</sub>	Brown	170	12.22 (12.99)	1.02 (0.96)	7.12 (7.81)	64.55 (63.50)	15.09 (15.12)
GeCl <sub>4</sub> (pym) <sub>2</sub>	White	120	25.65 (25.89)	2.15 (2.25)	14.96 (14.79)	37.84 (36.99)	—
SnCl <sub>4</sub> (apy) <sub>2</sub>	do	310	18.80 (17.08)	2.76 (2.56)	27.41 (25.98)	27.75 (27.59)	23.23 (23.95)
SnBr <sub>4</sub> (apy) <sub>2</sub>	Yellow	290	13.96 (14.88)	2.05 (2.33)	20.33 (19.81)	46.41 (47.11)	17.23 (17.14)
GeCl <sub>4</sub> (apy) <sub>2</sub>	Murky white	295(d)	20.68 (20.54)	3.03 (2.94)	30.13 (29.41)	30.51 (30.91)	—
SnCl <sub>4</sub> (pyl) <sub>2</sub>	Light yellow	215(d)	21.23 (20.19)	1.78 (1.24)	12.38 (11.39)	31.32 (31.12)	26.21 (25.81)
SnBr <sub>4</sub> (pyl) <sub>2</sub>	Yellow	208(d)	15.24 (14.99)	1.27 (1.25)	8.88 (8.47)	50.70 (49.13)	18.82 (17.99)
GeCl <sub>4</sub> (pyl) <sub>2</sub>	White	195	23.64 (23.60)	1.98 (1.89)	13.78 (13.01)	34.87 (33.99)	—
SnCl <sub>4</sub> (mpy) <sub>2</sub>	Dark brown	310(d)	17.64 (17.31)	2.22 (2.09)	20.56 (20.98)	26.02 (25.99)	21.78 (21.70)
SnBr <sub>4</sub> (mpy) <sub>2</sub>	Yellow	354	13.29 (13.21)	1.67 (1.61)	15.50 (15.40)	44.23 (44.99)	16.42 (15.98)
GeCl <sub>4</sub> (mpy) <sub>3</sub>	Brown	325	22.49 (22.81)	2.83 (3.26)	26.21 (26.60)	22.12 (21.35)	—
SnCl <sub>4</sub> .opy	White	>360	17.33 (17.01)	2.16 (2.13)	10.11 (9.90)	34.12 (34.11)	28.58 (27.76)
SnBr <sub>4</sub> .opy	Yellow	215(d)	12.13 (11.91)	1.52 (1.19)	7.08 (6.81)	53.87 (52.98)	20.01 (19.40)
GeCl <sub>4</sub> (opy) <sub>3</sub>	Light yellow	135	31.79 (32.01)	4.00 (3.85)	18.55 (17.83)	20.85 (19.91)	—

mercaptoform. The infrared spectra of its complexes are not very different from that of the ligand, except in the  $\nu\text{C}=\text{S}$  region. The  $\nu\text{C}=\text{S}$  at 1200 shifts to lower spectral region (1181-1175) in the spectra of the complexes indicating coordination through the thiocarbonyl sulphur atom.

**4-Amino-1,3-dimethyl-2,6-dioxypyrimidine complexes** — The  $\nu\text{C}=\text{O}$  at 1667 in the ligand remains unchanged in the complexes ruling out coordination through the oxygen atom. In all the complexes a decrease in the ring stretching frequencies (1608-1437) is attributable to coordination through the ring nitrogen<sup>15</sup>. In SnCl<sub>4</sub> and SnBr<sub>4</sub> complexes there is a marked decrease in  $\nu\text{N}-\text{H}$  (3500, 3322) indicating coordination through the amino group also.

**Far infrared data** — Pyrimidine does not have fundamentals below 346 to offer any interference in the region of metal-halogen and metal-nitrogen stretching vibrations. The  $\nu\text{M}-\text{X}$  bands have been identified by referring to previous data on pyrazine and other related systems<sup>16-19</sup>: SnCl<sub>4</sub>(pym)<sub>2</sub>, 334; SnBr<sub>4</sub>(pym)<sub>2</sub>, 238; GeCl<sub>4</sub>(pym)<sub>2</sub>, 348; SnCl<sub>4</sub>(apy)<sub>2</sub>, 290; SnBr<sub>4</sub>(apy)<sub>2</sub>, 216; GeCl<sub>4</sub>(apy)<sub>2</sub>, 356; SnCl<sub>4</sub>(pyl)<sub>2</sub>, 304; SnBr<sub>4</sub>(pyl)<sub>2</sub>, 218; GeCl<sub>4</sub>(pyl)<sub>2</sub>, 398; SnCl<sub>4</sub>(mpy)<sub>2</sub>, 340; SnBr<sub>4</sub>(mpy)<sub>2</sub>, 242; GeCl<sub>4</sub>(mpy)<sub>3</sub>, 430, 396; SnCl<sub>4</sub>.opy, 314; SnBr<sub>4</sub>.opy, 230 and GeCl<sub>4</sub>(opy)<sub>3</sub>, 414, 406. The  $\nu\text{Sn}-\text{I}$  band could not be observed in the spectral range studied. The bands which are virtually unaffected by changing halogen are attributed to  $\nu(\text{M}-\text{N})$  and  $\nu(\text{M}-\text{O})$  (M-N, 224-298 M-O, 553-574 cm<sup>-1</sup>). In complexes of apy and mpy

the  $\nu\text{M}-\text{N}$  and  $\nu\text{M}-\text{S}$  bands, respectively, could not be distinguished unambiguously from the ligand internal modes. In pyl complexes the 552-574 region bands have been assigned to  $\nu(\text{M}-\text{O})$  modes<sup>20</sup>.

In 1:2 (MX<sub>4</sub>: ligand) complexes the presence of only one M-X band is indicative of a *trans*-octahedral configuration<sup>16,21</sup>. The ligand must be monodentate in all the 1:2 complexes. In pym and apy complexes coordination should be occurring through any one of the two equivalent nitrogen atoms. Sn(IV) chloride and bromide complexes of opy obtained in a 1:1 ratio also have only one  $\nu\text{M}-\text{X}$  at 314 and 230 respectively. This is very close to their position in other hexacoordinated complexes of the present series and also in previously recorded pyrazine complexes<sup>16</sup>. The close similarity between the spectra of 1:2 and 1:1 complexes indicates that the complexes SnCl<sub>4</sub>.opy and SnBr<sub>4</sub>.opy also have a polymeric 6-coordinated *trans*-octahedral geometry with ligand bridging involving the amino group and one of the ring nitrogen atoms. The nitrogen atom should presumably be the one at position-1 if a linear polymer is being formed, however, the possibility of the formation of a non-linear polymer involving nitrogen at position-3 cannot be ruled out.

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