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### Complexes of Sn(IV), Ge(IV), Si(IV) & Ti(IV) Halides with Pyridazine

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Received 20 May 1976; accepted 23 August 1976

Preparation and characterization of complexes of the type  $\text{MX}_4(\text{Pyd})_n$  [for  $\text{M} = \text{Sn}$ ;  $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ;  $n = 1, 2$  and for  $\text{M} = \text{Ge}, \text{Si}, \text{Ti}$ ;  $\text{X} = \text{Cl}$ ;  $n = 2$ ] are reported. The far infrared spectra indicate a *trans*-octahedral environment for the metal ion with both bidentate ( $n = 1$ ) and unidentate ( $n = 2$ ) pyridazine ligands. A polymeric structure involving azine bridging is proposed for the 1:1 complexes.

**D**IАЗINES have been found to act as unidentate or bidentate ligands forming octahedral (monomeric or polymeric) complexes involving azine or/and halogen bridged structures<sup>1-5</sup>. Pyrazine (1,4-diazine) complexes of tin(IV) halides of the type  $\text{SnX}_4$  (pyrazine) and  $\text{SnX}_4(\text{pyrazine})_2$  have recently been reported and a *trans*-octahedral structure involving azine bridging in the 1:1 complexes and a terminal coordination of the ligand in the 1:2 complexes have been proposed<sup>6</sup>. In this paper we report the results of our studies on the pyridazine (1,2-diazine, Pyd) complexes of tetrahalides of group (IV) elements.

Tin(IV) halides were prepared according to standard methods<sup>7</sup>. Pyridazine (Pyd) and metal halides were commercial samples and were used as such. All manipulations were carried out in a dry box.

The infrared spectra were recorded on a Beckman IR-12 spectrophotometer in KBr (4000-650  $\text{cm}^{-1}$ ) and in nujol (650-200  $\text{cm}^{-1}$ ). Conductivity measurements were made on  $\text{Sn(IV)}$  complexes using a Systronix conductivity bridge type 302. Other complexes were insoluble in most of the organic solvents.

Complexes of the type  $\text{MX}_4(\text{Pyd})_2$  were prepared by mixing chloroform solutions of metal salt and the ligand in 1:2 (metal-ligand) ratio. Complexes of the type  $\text{MX}_4(\text{Pyd})$  were prepared by taking metal salt and ligand solutions in 2:1 ratio. In each case a solid product was obtained immediately, which was washed with the solvent and dried *in vacuo*. The characterization data of the complexes are listed in Table 1.

All the adducts except those of  $\text{SnCl}_4$  and  $\text{SnBr}_4$  are highly air- and moisture-sensitive. The molar conductivities of tin complexes in nitromethane ( $10^{-3}M$ ) are in the range 40-50  $\text{ohm}^{-1} \text{cm}^2 \text{mole}^{-1}$  indicating them to be non-electrolytes<sup>8</sup>.

Tentative geometries of the complexes have been deduced on the basis of far IR spectral studies. The ring vibrations of pyridazine observed at 624, 540 and 368  $\text{cm}^{-1}$  shift to higher frequency region in the complexes due to certain rigidity in the ligand

TABLE 1—COLOUR, MELTING POINTS AND ANALYTICAL DATA OF THE COMPLEXES

Complex	Colour	m.p. (°C)	Calc. (Found), %			
			C	H	N	X
$\text{SnCl}_4(\text{Pyd})_2$	White	295 (d)	22.85 (22.46)	1.91 (2.37)	13.32 (13.40)	33.70 (34.56)
$\text{SnCl}_4(\text{Pyd})$	do	260 (d)	14.11 (14.98)	1.18 (0.90)	8.23 (9.01)	41.63 (40.82)
$\text{SnBr}_4(\text{Pyd})_2$	do	195 (d)	16.05 (15.56)	1.34 (1.32)	9.36 (8.84)	53.39 (52.42)
$\text{SnBr}_4(\text{Pyd})$	Yellow	170 (d)	9.27 (9.98)	0.78 (1.10)	5.41 (5.89)	61.66 (60.12)
$\text{SnI}_4(\text{Pyd})_2$	Dark brown	110	12.22 (12.61)	1.02 (1.29)	7.12 (7.41)	64.55 (65.61)
$\text{SnI}_4(\text{Pyd})$	Dark green	125	6.80 (7.56)	0.57 (0.87)	3.97 (3.98)	71.86 (70.11)
$\text{GeCl}_4(\text{Pyd})_2$	Murky white	154	25.65 (25.62)	2.15 (2.83)	14.96 (15.31)	37.84 (38.01)
$\text{SiCl}_4(\text{Pyd})_2$	White	198 (d)	29.12 (28.91)	2.44 (2.54)	16.97 (17.88)	42.95 (42.40)
$\text{TiCl}_4(\text{Pyd})_2$	Murky white	230 (d)	27.48 (28.00)	2.30 (2.61)	16.02 (16.98)	40.52 (41.83)

molecule on account of complexation<sup>9</sup>. In all the complexes a new band appears at about 400 cm<sup>-1</sup> which may be due to the change of symmetry of the ligand molecule.

The  $\nu$ M-X bands which have been identified on the basis of previous IR data on pyrazine<sup>6</sup> and other related systems<sup>10-13</sup> are shifted to lower frequencies with increasing size of the halogen [SnCl<sub>4</sub>(Pyd)<sub>2</sub>, 338vs; SnCl<sub>4</sub>(Pyd), 332sh, 324vvs, b; SnBr<sub>4</sub>(Pyd)<sub>2</sub>, 244vvs; SnBr<sub>4</sub>(Pyd), 238vvs; SnI<sub>4</sub>(Pyd)<sub>2</sub>, <200; SnI<sub>4</sub>(Pyd), <200; GeCl<sub>4</sub>(Pyd)<sub>2</sub>, 382vs; SiCl<sub>4</sub>(Pyd)<sub>2</sub>, 455vs, b and TiCl<sub>4</sub>(Pyd)<sub>2</sub>, 416vs, b]. As expected, the magnitude of shift to lower frequency in the  $\nu$ M-Cl is in the order: Si>Ti>Ge>Sn. Since pyridazine does not have fundamentals below 368 cm<sup>-1</sup>, the new bands below this frequency are attributed to  $\nu$ M-N modes [SnCl<sub>4</sub>(Pyd)<sub>2</sub>, 232w; SnCl<sub>4</sub>(Pyd) 242w; SnI<sub>4</sub>(Pyd)<sub>2</sub>, 238w; SnI<sub>4</sub>(Pyd), 220w; GeCl<sub>4</sub>(Pyd)<sub>2</sub>, 270w; SiCl<sub>4</sub>(Pyd)<sub>2</sub>, 318w and TiCl<sub>4</sub>(Pyd)<sub>2</sub>, 288w]. The assignment of  $\nu$ Sn-N in SnBr<sub>4</sub> complexes is difficult because of overlapping by strong  $\nu$ Sn-Br absorptions<sup>6,13</sup>.

The presence of only one  $\nu$ M-X band in MX<sub>4</sub>(Pyd)<sub>2</sub> type of complexes is indicative of a *trans*-octahedral geometry (point group *D*<sub>4h</sub>)<sup>6,14</sup> involving monodentate pyridazine molecules. The identical position of  $\nu$ Sn-X in 1:1 and 1:2 complexes of tin(IV) indicates a similar environment in both the complexes<sup>6</sup>, thereby ruling out the possibility of 5-coordinated tin in the case of MX<sub>4</sub>(Pyd) complexes. Thus the latter complexes may also be six coordinated. To account for the octahedral stoichiometry for SnX<sub>4</sub>.Pyd the sixth site must be satisfied by a bridging halogen or a ligand molecule. The  $\nu$ M-X vibration should have shifted to lower frequency if halide bridging<sup>9</sup> were present. The SnX<sub>4</sub>(Pyd) complexes are, therefore, postulated as polymeric *trans*-octahedral compounds involving azine bridging.

It is, therefore, concluded that pyridazine in the 1:1 complexes acts as a bidentate ligand, whereas in the 1:2 complexes it is unidentate.

We are grateful to Prof. W. Rahman, Head, Department of Chemistry, for providing the necessary facilities. One of us (T.A.K.) acknowledges the financial assistance from the UGC, New Delhi.

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#### Transition Metal Complexes of 4-Phenyl-1-salicyloyl Thiosemicarbazide

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Received 29 March 1976; accepted 2 July 1976

Complexes of the formulae M(SPTSC-2H) [where M = oxovanadium(IV), Mn(II), Co(II), Ni(II), Cu(II) or Zn(II) and SPTSC = 4-phenyl-1-salicyloylthiosemi-

carbazide (C<sub>6</sub>H<sub>4</sub>OH-C-NH-NH-C-NH Ph)], Cu(SPTSC-H)Cl and Fe(SPTSC-2H)OH have been prepared. The molar conductances of the complexes in nitrobenzene show them to be non-electrolytes. Magnetic moments of the complexes have been measured and the bonding sites inferred from IR data.

WE have reported earlier the preparation and characterization of tin(IV) halide and first row transition metal complexes of 1,4-disubstituted thiosemicarbazides<sup>1-4</sup>. The synthesis and structural studies on the complexes of 4-phenyl-1-salicyloyl thiosemicarbazide (SPTSC) with some first row transition metal ions are reported in this note.

All the chemicals used were BDH reagents. SPTSC was prepared by the reaction of salicyloylhydrazine with phenyl isothiocyanate under reflux in ethanol, m.p. 184° (Found: N, 14.9. Calc.: N, 14.6%).

Complexes of the type M(SPTSC-2H) where M = oxovanadium(IV), Mn(II), Co(II) and Ni(II), Cu(SPTSC-H)Cl and Fe(SPTSC-2H)OH were prepared by adding an ethanolic or aqueous solution of metal salts (15 mmoles) to an ethanolic solution of SPTSC (10 mmoles).

Cu(SPTSC-2H) and Zn(SPTSC-2H) were prepared by mixing aqueous or ethanolic solutions of metal salts and ligand in 3:2 molar ratio and raising the pH by the addition of an aq. solution of sodium acetate.

The complexes were digested on a water-bath for 4 hr, filtered, washed with hot ethanol, dried *in vacuo* and analysed as described earlier<sup>3</sup> (Table 1).

All the complexes are insoluble in CHCl<sub>3</sub>, CCl<sub>4</sub> and pet. ether but soluble in donor solvents like pyridine and ethylene diamine and sparingly soluble in nitrobenzene. All complexes are non-electrolytes as is evident from their very low molar conductances (<1.5 cm<sup>2</sup> mho/mole) in nitrobenzene.

The Ni(II) complex is diamagnetic and hence square-planar geometry may be assigned to it. The  $\mu_{\text{eff}}$  value of Co(SPTSC-2H) is well within the range expected for the square-planar Co(II) complexes<sup>5</sup> (Table 1). The subnormal magnetic moments