NOTES

20. Figgis, B. N. Personal communication.

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 MX₄ (pyridazine)ₙ [for M = Sn; X = Cl, Br, I; n = 1, 2 and for M = Ge, Si, Ti; X = 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.

DIAZINES have been found to act as unidentate or bidentate ligands forming octahedral (monomeric or polymeric) complexes involving azine or halogen bridged structures. Pyrazine (1,4-diazine) complexes of tin(IV) halides of the type SnX₄ (pyrazine) and SnX₄ (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. In this paper we report the results of our studies on the pyridazine (1,2-diazine, Pyd) complexes of tetrahalides of group (IV) elements.

The infrared spectra were recorded on a Beckman IR-12 spectrophotometer in KBr (4000-650 cm⁻¹) and in nujol (650-200 cm⁻¹). Conductivity measurements were made on SnX₄ (pyridazine) complexes using a Systronix conductivity bridge type 302. Other complexes were insoluble in most of the organic solvents.

Complexes of the type MX₄(Pyd)₂ were prepared by mixing chloroform solutions of metal salt and the ligand in 1:2 (metal-ligand) ratio. Complexes of the type MX₄(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 SnCl₄ and SnBr₄ are highly air- and moisture-sensitive. The molar conductivities of tin complexes in nitromethane (10⁻³ M) are in the range 40-50 ohm⁻¹ cm² mole⁻¹, indicating them to be non-electrolytes.

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 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

<table>
<thead>
<tr>
<th>Complex</th>
<th>Colour</th>
<th>m.p. (°C)</th>
<th>Calc. (Found), %</th>
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| SnCl₄(Pyd)₂ | White          | 295 (d)  | 22:85%
|             |                |          | (22:46)   | 1:91   | 13:32   | 33:70      |
| SnCl₄(Pyd)  | do             | 260 (d)  | 14:11%     | 1:18   | 8:23   | 41:63      |
| SnBr₄(Pyd)  | do             | 195 (d)  | (14:98)    | 0:90   | 9:01   | (40:82)   |
| SnBr₄(Pyd)  | Yellow         | 170 (d)  | 16:05%     | 1:34   | 9:36   | 53:39      |
|             |                |          | (15:56)    | 1:32   | (8:84) | (52:42)   |
|              |                |          | 9:27       | 0:78   | 5:41   | 61:66      |
| SnI₄(Pyd)   | Dark brown     | 110      | (9:98)     | 1:10   | (5:89) | (60:12)   |
| SnI₄(Pyd)   | Dark green     | 125      | 12:22      | 1:02   | 7:12   | 64:55      |
| GeCl₄(Pyd)₂ | Murky white    | 154      | (12:61)    | 1:29   | (4:71) | (65:61)   |
| SiCl₄(Pyd)  | White          | 198 (d)  | 6:80       | 0:57   | 3:97   | 71:96      |
| TiCl₄(Pyd)₂ | Murky white    | 230 (d)  | (7:56)     | 0:87   | (3:98) | (70:11)   |
|             |                |          | (25:65)    | 2:15   | 14:96  | 37:94      |
|             |                |          | (25:62)    | 2:83   | (15:31) | 38:01      |
|             |                |          | 29:12      | 2:44   | 16:97  | 40:55      |
|             |                |          | (28:91)    | 2:54   | (17:88) | (42:40)    |
|             |                |          | (27:48)    | 2:30   | 16:02  | 40:32      |
|             |                |          | (28:00)    | 2:61   | (16:98) | (41:83)    |
molecule on account of complexation. In all the complexes a new band appears at about 400 cm⁻¹ which may be due to the change of symmetry of the ligand molecule.

The νM-X bands which have been identified on the basis of previous IR data on pyrazine and other related systems⁷⁻¹³ are shifted to lower frequencies with increasing size of the halogen [SnCl₄(Pyd)₂, 335 vs; SnCl₄(Pyd), 322, 324 vs; b; SnBr₄(Pyd)₂, 244 vs; SnBr₄(Pyd), 238 vs; SnI₄(Pyd), < 200; SnI₄(Pyd), < 200; GeCl₄(Pyd), 382 vs; SiCl₄(Pyd), 455 vs; b and TiCl₄(Pyd), 416 vs]. As expected, the magnitude of shift to lower frequency in the νM-Cl is in the order: Si > Ti > Ge > Sn. Since pyridazine does not have fundamentals below 368 cm⁻¹, the new bands below this frequency are attributed to νM-N modes [SnCl₄(Pyd)₂, 232 w; SnCl₄(Pyd), 242 w; SnCl₄(Pyd), 238 w; SnCl₄(Pyd), 220 w; GeCl₄(Pyd), 270 w; SiCl₄(Pyd), 318 w and TiCl₄(Pyd), 288 w]. The assignment of νsN-N in SnBr₄ complexes is difficult because of overlapping with νsN-Br absorptions.⁷⁻¹³

The presence of only one νM-X band in MX₄(Pyd) type of complexes is indicative of a trans-occtahedral geometry (point group D₆h)⁶,¹⁴ involving monodentate pyridazine molecules. The identical νsM-X bands which have been identified on MX₄(Pyd), 373 and MX₄(Pyd), 368 m⁻¹, the new bands below this frequency are attributed to νM-O vibrations should have shifted to lower frequency for MX₄(Pyd), 242 w; SnCl₄(Pyd), 238 w; SnCl₄(Pyd), 220 w; GeCl₄(Pyd), 270 w; SiCl₄(Pyd), 318 w and TiCl₄(Pyd), 288 w]. The assignment of νsN-N in SnBr₄ complexes is difficult because of overlapping with νsN-Br absorptions.⁷⁻¹³

§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-salicyloylthiosemicarbazide(C₆H₅OH-C-NH-CN-CN-CN-Ph)] were 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.⁵⁴ 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 reacting of salicyloylhydrazine with phenyl isothiocyanate under reflux in ethanoate, 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 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.

References