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 vM-X bands which have been identified on the basis of previous IR data on pyrazine and other related systems are shifted to lower frequencies with increasing size of the halogen [SnCl$_4$ (Pyd)$_2$, 338 vs; SnCl$_4$(Pyd), 332 sh, 324 vvs, b; SnBr$_4$ (Pyd)$_2$, 244 vvs; SnBr$_4$(Pyd), 238 vs; SnI$_4$(Pyd)$_2$, <200; SnI$_4$(Pyd), <200; GeCl$_4$(Pyd)$_2$, 382 vs; SiCl$_4$ (Pyd)$_2$, 455 vvs, b and TiCl$_4$(Pyd)$_2$, 416 vs,b]. As expected, the magnitude of shift to lower frequency in the vM-Cl is in the order: Si>Ti>Ge>Sn. Since pyridazine does not have fundamentals below 300 cm$^{-1}$, the new bands below this frequency are attributed to vM-N modes [SnCl$_4$(Pyd)$_2$, 232 w; SnCl$_4$(Pyd), 242 w; SnI$_4$(Pyd)$_2$, 238 w; SnI$_4$(Pyd), 220 w; GeCl$_4$(Pyd)$_2$, 270 w; SiCl$_4$(Pyd)$_2$, 318 w and TiCl$_4$(Pyd)$_2$, 288 w]. The assignment of vSn-N in SnBr$_4$ complexes is difficult because of overlapping by strong vSn-Br absorptions.

The presence of only one vM-X band in MX$_4$ (Pyd)$_2$ type of complexes is indicative of a trans-octahedral geometry (point group D$_{4h}$) involving monodentate pyridazine molecules. The identical position of only one vSn-X in 1:1 and 1:2 complexes of the ligand molecule.

We have reported earlier the preparative and characterization of tin(iv) halide and first row transition metal complexes of 1,4-disubstituted thiosemicarbazides. The synthesis and structural studies on the complexes of 4-phenyl-1-saliciloyl thiosemicarbazide (SPTSC) with some first transition metal ions are reported in this note.

All the chemicals used were BDH reagents. SPTSC was prepared by the reaction of salicyloyl hydrazine with phenyl isothiocyanate under reflux in ethanol, m.p. 1840 (Found: N, 14.9. Calc.: N, 14.6%).

Complexes of the type M(SPTSC-2H)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.

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observed for Fe(II), oxovanadium(IV) and Cu(II) complexes may be explained by assuming hydroxobridging interactions of the type V=O...V (ref. 7) and metal-metal interactions respectively.

The 3350 cm\(^{-1}\) band in the IR spectrum of SPTSC (nujol) is assigned to the \(\nu\)O-H (phenolic) which disappears in the spectra of all the complexes except Cu(SPTSC-H)Cl, indicating coordination through phenolic oxygen. The \(\nu\)N-H band at 3300 cm\(^{-1}\) in the solution spectrum of the ligand suffers a negative shift in all the complexes indicating the involvement of one or more >N-H groups in coordination. This band, however, disappears in all the other complexes, suggesting the enolization of keto group.

The \(\nu\)=S occurring at 1338 cm\(^{-1}\) in the spectrum of SPTSC remains unaltered in Cu(SPTSC-H)Cl indicating that the carbonyl group is not taking part in coordination in this complex. This band, however, disappears in all the other complexes, suggesting the enolization of keto group.

\(\nu\)N-N occurring at 900 cm\(^{-1}\) in the spectrum of SPTSC shifts to the higher frequency side in all the complexes. The magnitude of the positive shift suggests the involvement of one of the hydradzinic nitrogens in bonding.

The non-ligand bands occurring in the regions 450-400, 385-308, 330-280 and 850 cm\(^{-1}\) in the spectra of complexes may be tentatively assigned to \(\nu\)M-O (ref. 11-13) \(\nu\)M-S (ref. 11, 14) \(\nu\)M-N (ref. 12, 15, 16) and \(\nu\) Fe-O-Fe (ref. 6) modes respectively.

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References

Organotin(IV) & Organoxytitanium(IV) Diphenyl Phosphinates*

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Organotin(IV) phosphinates of the formula \(R_2SnL_2\) and \(R_3SnL\) (\(R =\) butyl, phenyl, benzyl; \(L =\) diphenyl phosphinic acid) have been prepared from the respective chlorotin compound and sodio-derivative of the ligand. Organic chelating ligands (salicylaldehyde, acetyl acetone, 8-hydroxyquinoline) replace the alkoxy groups of disopropoxy titanium bis-diphenyl phosphinate giving new chelated titanium compounds in which both the isopropoxy groups are replaced by the ligands.

ORGANOMETALLIC compounds containing Sn-O-P and Ti-O-P linkages have attracted considerable attention. A number of titanium

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