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Pyrazole, 3(5)-Methyl Pyrazole and 3,5-Dimethyl Pyrazole Complexes of Tin(IV) Halides

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Complexes of tin(IV) halides with pyrazole, 3(5)-methyl pyrazole and 3,5-dimethyl pyrazole of the type $SnX_4 \cdot L_2$ were prepared. All the isolated solids were non-electrolytes in acetonitrile. The IR spectra of the complexes (600–180 cm^{-1}) were consistent with a trans*-octahedral configuration in the solid state. The dipole moment data suggest that this configuration remains in solution.*

Introduction

The coordination chemistry of the Sn(IV) halides has been reviewed recently [1] and the *cis–trans* isomerism in compounds of the type $SnX_4 \cdot L_2$ is one of the most interesting fields [2–4].

In a previous paper [5] the interaction of SnX_4 with imidazole and derivatives has been studied, and this investigation is extended now to nitrogen donors like pyrazoles. The coordination chemistry of these bases has been the subject of recent reviews [6, 7] in which their interaction with transition metals has mainly been studied.

In this paper, isolation and study of SnX_4 (where X = Cl, Br, I) complexes with pyrazole (Pz), 3(5)-methyl pyrazole (MPz) and 3,5-dimethyl pyrazole (DMPz) are described.

Experimental

Materials

Pyrazole Merck synthesis grade, tin tetrabromide and tetraiodide Merck have been utilized without further purification. 3,5-Dimethyl pyrazole Ega 99% was purified by recrystallization from benzene, 3(5)-methyl pyrazole Ega 98% and tin tetrachloride Merck by vacuum distillation. Benzene Carlo Erba for spectrophotometry used in dielectrometric measurements was stored over molecular sieves 4Å. The other solvents were purified by usual methods.

Preparation of Complexes

The adducts $SnX_4 \cdot L_2$ were prepared in benzene by mixing solutions containing the acceptor and the donor in a proportion slightly higher than the 1:2 acceptor/donor molar ratio (MR). When $SnCl_4$ or $SnBr_4$ was the acceptor liberation of heat was observed. The reaction of SnI_4 with MPz afforded an oil. This was concentrated and cooled until a solid was formed. The isolated adducts were washed with benzene and vacuum dried. An attempt to prepare $SnI_4(DMPz)_2$ was unsuccessful.

TABLE I. Analytical and Some Other Physical Data of the Prepared Compounds.

Compound	Colour	M.P. (°C)	% Sn	% C	% N	% H
$SnCl_4(Pz)_2$	White	280^a	29.15 (29.94)^b	18.11 (18.16)	14.00 (14.12)	1.84 (2.02)
$SnBr_4(Pz)_2$	White	190^a	20.43 (20.67)	12.68 (12.54)	9.92 (9.75)	1.24 (1.39)
$SnI_4(Pz)_2$	Brown	120^a	15.08 (15.57)	9.42 (9.44)	7.50 (7.34)	0.86 (1.05)
$SnCl_4(MPz)_2$	White	280^a	27.52 (27.96)	22.54 (22.61)	13.18 (13.19)	2.60 (2.83)
$SnBr_4(MPz)_2$	White	250^a	19.43 (19.71)	16.35 (15.94)	9.71 (9.30)	1.90 (1.99)
$SnI_4(MPz)_2$	Brown	170	14.75 (15.02)	12.13 (12.15)	7.39 (7.09)	1.31 (1.52)
$SnCl_4(DMPz)_2$	White	250^a	25.98 (26.23)	25.85 (26.52)	12.36 (12.37)	3.03 (3.53)
$SnBr_4(DMPz)_2$	Yellow	220^a	18.10 (18.83)	17.93 (19.04)	8.93 (8.88)	2.27 (2.54)

^{a} Decomposition. ^{b} Theoretical percentage is given in brackets.

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Analytical Results

C, N, H were determined with a Perkin–Elmer 240 apparatus. Tin was determined gravimetrically as SnO_2. The analytical results, the colour and the melting points of the adducts are given in Table I.

Physical Measurements

Melting points (uncorrected) were determined using a Büchi apparatus. Conductometric studies were carried out employing the apparata described in a previous paper [8]. Dipole moments were determined at 25 °C by the method previously described [9], or using dielectrometric titrations and refractometric index measurements [10, 11]. Molecular weight of $SnI_4(Pz)_2$ was determined in benzene at 37 °C using a Hitachi–Perkin Elmer 115 apparatus. The IR spectra were recorded in potassium bromide pellets or Nujol mulls between NaCl (4000–600 cm^{-1}) or polyethylene (600–180 cm^{-1}) windows using a Perkin–Elmer 180 spectrophotometer. As far as possible, a dry box was used for manipulations.

Results and Discussion

All the prepared compounds are solids, slightly stable to moisture. They are soluble in ethanol and acetone and less soluble in benzene, dioxane, cyclohexane and carbon tetrachloride. Their molar conductivity at 10^{-3}*M* in acetonitrile (*e.g.* 9.3 ohm^{-1} cm^2 mol^{-1} for $SnCl_4(Pz)_2$) shows a non-electrolyte behaviour in this solvent [12].

The IR measurements were centred in the study of the halogen–metal and metal–ligand bands, and in the modifications of the ligand bands by coordination.

The ligand bands were assigned as previously [13–15]. A large upfield shift in the N–H stretch compared to liquid or solid ligand is observed upon coordination (Table II). This shift is downfield compared to the gaseous ligand and to a dilute solution of the ligand (3541 cm^{-1} for Pz gas [13], 3536 cm^{-1} for MPz gas [14] and 3485 cm^{-1} for DMPz in CCl_4 solution [16]), and can be attributed to a moderately strong hydrogen bonding between the N–H group and halogen atoms from the same or neighbouring tin atoms. This fact has been also observed in the adducts $(CH_3)_2SnX_2\cdot 2DMPz$ [17].

On the other hand, ring stretching bands (1540–1360 cm^{-1} for Pz, 1575–1310 cm^{-1} for MPz and 1590–1300 cm^{-1} for DMPz) undergo shifts towards higher wavenumber generally smaller than 25 cm^{-1} so that they are not given in Table II. This fact shows that coordination involves the pyridine-type nitrogen [7] and shows a very slight modification in the ring structure as well, so that the parameters of free ligand can be used in structural discussions.

Table II also includes the ν_{Sn-X} modes. The existence of only one strong band in $SnCl_4(Pz)_2$, $SnBr_4(Pz)_2$, $SnCl_4(MP_2)_2$, $SnBr_4(MPz)_2$ and $SnBr_4(DMPz)_2$ suggests a *trans*-octahedral structure for these compounds. The range of operation of the IR spectrophotometer allows no conclusions in this way for the SnI_4 compounds.

The two bands shown for $SnCl_4(DMPz)_2$ do not suggest, in a first consideration, a *trans* configuration for this compound. However, the *cis* isomer must be rejected, because this structure exhibits a more complicated spectrum (*e.g.* 333, 327, 321 and 283 cm^{-1} as Sn–Cl stretching modes in $SnCl_4(bipy)$ [3]). On the other hand, the studies carried out on *trans*-$SnCl_4(py)_2$ [3] showed that the ν_{Sn-Cl} band has a shoulder located at about 305 cm^{-1}. This shoulder was assigned to a splitting of the E_u mode due to a reduction of the D_{4h} symmetry in the solid state. A similar phenomenon occurs in $SnBr_4(py)_2$, and the two bands at 246 cm^{-1} and 230 cm^{-1} were attributed to a D_{2h} symmetry generated by the non-free rotation of the ligand around the Sn–N axis in the *trans* compound. Thus, the two bands in $SnCl_4(DMPz)_2$ may be due to a similar effect and the structure of this adduct would be a *trans* configuration.

TABLE II. Infrared Bands (cm^{-1}) of Ligands and Complexes.

Compound	ν_{N-H}	ν_{Sn-X}	ν_{Sn-N}	Other Bands (range 500–180 cm^{-1})		
Pz	2900 vs	–	–	–	–	–
$SnCl_4(Pz)_2$	3340 vs	322 vs	245 m	225 sh	189 w	–
$SnBr_4(Pz)_2$	3340 vs	230 vs	250 s	210 sh	–	–
$SnI_4(Pz)_2$	3320 vs	185 vs	220 m	–	–	–
MPz	3180 vs	–	–	350 w	278 w	–
$SnCl_4(MPz)_2$	3330 vs	322 vs	–	370 w	287 w	209 w
$SnBr_4(MPz)_2$	3340 vs	230 vs	–	365 w	300 w	205 sh
$SnI_4(MPz)_2$	3340 vs	188 vs	–	360 w	–	200 sh
DMPz	3200 vs	–	–	403 s	270 m	228 m
$SnCl_4(DMPz)_2$	3340 vs	338 vs, 322 vs	–	435 m	300 m	195 m
$SnBr_4(DMPz)_2$	3345 vs	232 vs	–	435 m	295 m	195 s

The assignment of the Sn–N bands is more tentative and has been carried out in the pyrazole compounds because this ligand has no bands in this zone. Their position follows the same sequence which was observed for $VCl_2(py)_4$ and $VCl_2(Pz)_4$ [3, 18]. On the other hand, the non-splitting of these bands contributes to confirm the suggested *trans*-configuration. The bands around 200 cm^{-1} in DMPz and MPz complexes (Table II) could be assigned to Sn–N stretching; however, the free ligands have some bands in this range, so they could be considered either ligand modes or Sn–N stretching.

Although *trans*-configuration complexes can display dipole moments different from zero when the direction of the ligand dipole moment does not coincide with the direction of the coordinate metal–ligand bond (as in our case) [19], if the found moment is low enough *cis*-configuration can be excluded. For this reason, the determination of dipole moments of the complexes in benzene and dioxane was attempted, this determination being strongly conditioned by the low solubility of all adducts in these solvents. The found values for the complexes are given in Table III. Only two of them have been obtained by dielectrometric titrations in dioxane (Fig. 1), so these values can be considered as being free of dissociative phenomena such as:

$$SnX_4 \cdot L_2 \rightleftharpoons SnX_4 \cdot L + L \qquad (1)$$

TABLE III. Dipole Moments (Debyes) of Some Complexes.

Compound	μ (Direct)	μ (Dielect. Titration)
$SnI_4(Pz)_2$	4.0 (B)[b]	–
$SnBr_4(MPz)_2$	5.2 (D)	3.3 (D)[a]
$SnI_4(MPz)_2$	6.4 (B)	–
$SnCl_4(DMPz)_2$	–	3.3 (D)[a]

[a] The dielectrometric titrations gave a dipole moment for 1:1 complexes of 5.0 (bromide) and 6.1 (chloride). [b] B = benzene; D = dioxane.

The dipole moments directly obtained (Table III) are probably affected by these phenomena. This was proved in $SnI_4(Pz)_2$ whose molecular weight was determined in benzene (theoretical value = 762.3; experimental value = 584.2) and in $SnBr_4(MPz)_2$ in which its direct determination and dielectrometric titration were possible. The dipole moment of the 1:1 complex found by that titration (5.0 D) (Table III) is in agreement with the direct measurement; this seems to suggest that for this adduct, in dioxane, the equilibrium (1) has shifted to the right.

On the other hand, the dipole moments slightly higher than 3 D, found for $SnCl_4(DMPz)_2$ and $SnBr_4(MPz)_2$, excluded *cis* configurations because these structures would cause higher dipole moments. In fact, a moment between 7 and 9 D (depending on the position of the Pz rings relative to the plane determined by the I and Sn atoms) can be calculated for the *cis*-$SnI_4(Pz)_2$, if we assume: a) a regular octahedral structure in the adduct; b) a Sn–I bond moment of 2 D (estimated through the variation of this bond moment in the Sn–iodomethylated compounds [20, 21]; c) a donor moment $\mu = 2.3$ D [22]; d) an angle of 24° between the resultant moment of the donor and the direction of the Sn–N bond (calculated from the vectorial model suggested for Pz [23] using the dipole moments of pyrrol and pyridine in dioxane [22]); e) a donor–acceptor bond moment of 2 D (an acceptable value according to [10]). The $SnBr_4$ and $SnCl_4$ complexes would have even higher moments.

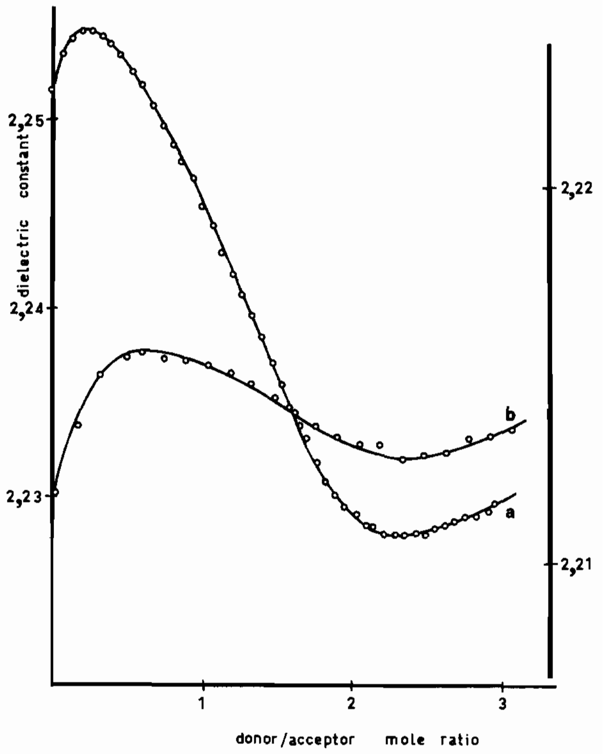

Figure 1. Dielectrometric titrations in dioxane of $SnBr_4$ with MPz (a) and $SnCl_4$ with DMPz (b). The right ordinate axis is for curve (b). The concentration of initial acceptor solutions is between 2.19×10^{-3} *M* and 1.06×10^{-2} *M*.

Consequently, we can suppose a *trans*-octahedral structure as the one belonging to the predominant species in dioxane solution for $SnCl_4(DMPz)_2$ and $SnBr_4(MPz)_2$, in spite of its having a non-zero value for the dipole moment. We should note that similar values have been found in Tl(III) and In(III) adducts, and they have been attributed to symmetric structures [24, 25]. This dipole moment can be attributed, in this case, to a non-symmetric disposition of the donor molecules, to an inadequate evaluation of the atomic polarization and to small phenomena of hydrolysis. the elimination of which is very difficult in dioxane solutions, even when working in a dry box.

These experimental results have been considered on the basis of the Zahrobsky procedure [26]. The construction of models from structural parameters [26–29] allows the classification of these compounds to the group of bulky ligands, similar in behaviour to pyridine, with a tendency to form *trans* configuration compounds with SnX_4 halides.

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