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Complexes of Some Group(IV) Metal Halides with 5-Aminoindazole

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The synthesis and characterisation of Sn(IV) halides, Ge(IV), Ti(IV) and Zr(IV) chloride complexes of the type $\text{MX}_4 \cdot \text{L}_{1-2}$ with 5-aminoindazole has been made. The possible structure of these complexes has been proposed on the basis of elemental analysis and infrared spectroscopy. The IR spectra suggest unidentate behaviour of the ligand involving pyrrole nitrogen in all the cases except the tin(IV) bromide complex, where the ligand exhibits its bidentate nature, involving the pyridyl nitrogen. An octahedral geometry has been proposed for all the complexes. In the case of $\text{MX}_4 \cdot \text{L}$ type complexes, except for $\text{SnBr}_4 \cdot \text{L}$, an octahedral halogen bridged structure has been proposed.

INTRODUCTION

A variety of indazole derivatives have been used as corrosion inhibitor and in the preparation of several types of dyes¹⁻³. Indazole and substituted indazoles have only recently been used as complexing ligand. A detailed study of the complexing behaviour of indazole derivatives has been reported from these laboratories⁴⁻⁸. In continuation of our earlier work on indazole and substituted indazoles with transition metal ions and with group(IV) metal halides, we are reporting here the study of 5-aminoindazole complexes (5-AInz.) with germanium(IV), titanium(IV), zirconium(IV) chloride and tin(IV) halides.

EXPERIMENTAL

Materials and Methods

Tin(IV) halides were prepared according to the standard methods (9). 5-Aminoindazole (Koch-Light m.p. 175 °C), GeCl_4 (Koch-Light) ZrCl_4 , and TiCl_4 (both B. D. H. reagents) were used as such.

Elemental analyses were made by microanalytical techniques and the estimation of halogen and metal was carried out gravimetrically (Table I). Conductance measurements were carried out on a »Systronix« conductivity bridge type 301-1. The infrared spectra ($4000-200 \text{ cm}^{-1}$) were recorded on a Perkin Elmer, 621 spectrophotometer. All the manipulation were carried out in a dry box under an atmosphere of dry nitrogen. Complexes were dried in a vacuum dessiccator over CaCl_2 .

Preparation of the Complexes

The complexes were prepared by mixing the ligand solution (in alcohol or chloroform) to the metal halides solution in the same solvent in 1 : 2 (M : L) ratio.

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TABLE I
Analytical Data and Some Physical Properties of the Complexes

Complex	Colour	M. P. ° C	%C		%H		%N		%M		%OX	
			Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
SnCl ₄ (5-AInz) ₂	Brown	275	31.45	(31.90)	2.05	(2.65)	15.75	(15.95)	22.49	(22.54)	26.72	(26.93)
SnBr ₄ (5-AInz)	Brick red	230	14.55	(14.70)	1.01	(1.22)	7.21	(7.35)	20.22	(20.77)		
SnI ₄ (5-AInz) ₂	Black	250	18.41	(18.82)	1.43	(1.56)	9.01	(9.41)	12.60	(13.30)		
ZrCl ₄ (5-AInz) ₂	Greenish white	360 d	33.01	(33.66)	2.71	(2.80)	16.70	(16.83)			28.50	(28.41)
GeCl ₄ (5-AInz)	Light brown	295	23.95	(24.18)	1.91	(2.01)	12.50	(12.09)			40.65	(40.81)
TiCl ₄ (5-AInz)	Brown	320 d	25.75	(26.03)	1.87	(2.16)	13.15	(13.01)			43.95	(43.94)

d = Decomposition temperature.

In each case a solid product was obtained after keeping the reaction mixture for a few hours, which was thoroughly washed with the solvent and dried in vacuum. A 1:2 complex in the case of SnCl_4 , SnI_4 and ZrCl_4 was obtained whereas SnBr_4 , GeCl_4 and TiCl_4 yielded only a 1:1 adduct, irrespective of the ratio of reacting components.

RESULTS AND DISCUSSION

The analytical results of the complexes (Table I) support the proposed stoichiometries. The molar conductivities of tin(IV) halide complexes in D.M.F. fall fairly below those quoted for univalent electrolytes. The conductance of the other complexes could not be measured because of their insolubility in any suitable solvent. The ligand, 5-aminoindazole has three donor sites, namely, the amino(NH_2), the pyrrole (NH) and the pyridiyl(N) nitrogen atom capable of coordinating with the metal ion. It was of interest to decide the coordination sites on the basis of the change in the group frequencies and also to see if 5-aminoindazole acted as a multidentate ligand. The possibility of the formation of polymeric species has also been considered. Since there are two potential coordination sites having an (N—H) group in the molecule, either one or both of these sites may be involved in coordination.

The infrared spectrum of 5-aminoindazole was reported earlier from this laboratory⁴. It shows a strong symmetric ν (N—H) band at 3200 cm^{-1} . It has not been possible to distinguish between the primary asymmetric (N—H) stretching frequency from the secondary symmetric (N—H) stretching frequency, i. e. ν (N—H) frequency of the pyrrole group. The spectrum of 5-aminoindazole in solution could not be recorded due to its insolubility in a suitable solvent. However, the spectrum of indazole in solution shows ν (N—H) at 3450 cm^{-1} which is due to non-hydrogen bonded ligand. A strong band at 1588 cm^{-1} is assigned to the (C=N) stretching frequency.

In all the complexes the (N—H) stretching frequency has been observed in the range $3320\text{--}3150\text{ cm}^{-1}$ (Table II) and is negatively shifted from its position in the free ligand. This distinct negative shift in (N—H) stretching frequency shows that the (N—H) group is participating in coordination. Of

TABLE II

Important IR Frequencies of the Ligand and the Complexes and Their Assignments

Complex	ν (N—H)/ cm^{-1}	ν (C—N)/ cm^{-1}	ν (M—N)/ cm^{-1}	ν (M—Cl)/ cm^{-1}
5-AInz	3350 m 3200 sh	1516 s	—	—
$\text{SnCl}_4(5\text{-AInz})_2$	3200 m, b	1510 s	425 s	320 s
$\text{SnBr}_4(5\text{-AInz})$	3320 m	1480 s	420 m	260 w
$\text{SnI}_4(5\text{-AInz})_2$	3240 m, b	1500 s	405 m	—
$\text{GeCl}_4(5\text{-AInz})$	3220 m	1490 m	440 m, b	330 vs 260 w
$\text{ZrCl}_4(5\text{-AInz})_2$	3300 sh, b	1495 s	—	—
$\text{TiCl}_4(5\text{-AInz})$	3160 s, b	1495 s	450 s	395 m, b 310 w

the two coordination sites having an (N—H) group, it has been observed that the pyrrole nitrogen is more susceptible to coordination than the amino nitrogen, nevertheless the coordination via the amino group may not be entirely ruled out¹⁰. The $\nu(\text{C}=\text{N})$ in all the complexes remained virtually unchanged or very slightly shifted, except in $\text{SnBr}_4 \cdot (5\text{-AInz})$.

The $\nu(\text{C}=\text{N})$ in $\text{SnBr}_4 \cdot (5\text{-AInz})$ has been found to be shifted to 1480 cm^{-1} from its position at 1516 cm^{-1} in free 5-AInz which tempts us to believe that both the pyrrole and pyridyl nitrogens are coordinated. In other cases the shift in $\nu(\text{C}=\text{N})$ is not significant. Similar results for the compounds of other indazole derivatives have also been reported⁷⁻⁸.

Low frequency i. r. spectra have been recorded with a view to distinguishing between the terminal $\nu(\text{M}-\text{X})$ and the bridging $(\text{M}-\text{X}-\text{M})$ stretching vibrations and also to locate the metal ligand vibrations. The $\nu(\text{M}-\text{X})$ usually appears as a strong band and shifts to a lower frequency region with increasing size of the halogen. The other $\text{M}-\text{X}$ bands are not pure absorption bands and hence probably appear at a slightly higher wave number.

A set of two $(\text{M}-\text{X})$ bands have been observed at 330 and 260 cm^{-1} for GeCl_4 and for TiCl_4 complex at 395 and 310 cm^{-1} . The first of these has been attributed to the terminal $\nu(\text{M}-\text{X})$ and the second to the bridging $\nu(\text{M}-\text{X}-\text{M})$ ¹¹. Thus we are encountering dimeric $\text{GeCl}_4 \cdot (5\text{-AInz})$, $\text{TiCl}_4 \cdot (5\text{-AInz})$ and $\text{SnBr}_4 \cdot (5\text{-AInz})$ complexes, and octahedral $\text{SnCl}_4 \cdot (5\text{-AInz})_2$, $\text{SnI}_4 \cdot (5\text{-AInz})_2$ and $\text{ZrCl}_4 \cdot (5\text{-AInz})_2$ complexes. New bands appearing in the $405\text{--}450 \text{ cm}^{-1}$ region in all the complexes have been assigned to $\nu(\text{M}-\text{N})$.

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SAŽETAK

Kompleksi nekih halida metala grupe (IV) s 5-aminoindazolom

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Sintetizirani su i karakterizirani kompleksi Sn(IV) halida, Ge(IV), Ti(IV) i Zr(IV) klorida tipa $\text{MX}_4 \cdot \text{L}_{1-2}$ s 5-aminoindazolom. Moguće strukture su predložene na temelju elementarne analize i IR spektara. IR spektri ukazuju na monodentatno

ponašanje liganda preko dušika u pirolskom prstenu u svim slučajevima osim Sn(IV) bromid kompleksa u kojem je opažena bidentatna priroda piridil-dušika. Za sve komplekse smatra se da imaju oktaedarsku strukturu. U svim MX_4 kompleksima, osim $SnBr_4 \cdot L$, predviđa se oktaedarska struktura s premoštenjem preko halogena.

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