

## SHORT COMMUNICATIONS

### IR SPECTROSCOPIC STUDIES OF SOME NON-TRANSITION METAL COMPLEXES

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**ABSTRACT.** preparation and characterization of Ge(IV), Sn(IV), Ti(IV) and Zr(IV) halide complexes of 5-aminoindazolethiocarbamate (5-Aidtc) are described. The low frequency IR spectra indicate an octahedral geometry in all the complexes involving bidentate ligands. A cis-octahedral structure is proposed for  $TiCl_4$  and  $GeCl_4$  complexes, whereas, a trans-octahedral structure is suggested for  $ZrCl_2(5-Aidtc)_2$ . A polymeric structure involving halogen bridges is proposed for  $SnX_3(5-Aidtc)$  (where X = Cl, Br or I) complexes.

### INTRODUCTION

The coordination chemistry of dithiocarbamates has been extensively studied (1-6). A new dithiocarbamate of 5-aminoindazole and its complexes with transition metals have recently been reported (7). However, there is no report of complex formation of Group(IV) metal halides with 5-aminoindazolethiocarbamate. In continuation of the earlier work on indazoles, substituted indazoles and dithiocarbamates (8-14), it was therefore of interest to synthesize and characterize the complexes of some Group(IV) metal halides namely Ge(IV), Ti(IV), Zr(IV) chlorides and Sn(IV) halides, with sodium 5-aminoindazolethiocarbamate with a view to exploring the possibility of formation of polymeric chelated species or monomeric species.

### EXPERIMENTAL

**Material and methods.** 5-Aminoindazole,  $GeCl_4$  (Aldrich),  $ZrCl_4$ ,  $TiCl_4$ , and tin(IV) halides (B.D.H.) were used as received without further purification. Elemental analyses were performed at A.M.U. Aligarh India. Halogen, sulphur and metals were analysed by literature methods (15-16). Infrared spectra ( $4000-650\text{ cm}^{-1}$ ) were recorded on a Perkin Elmer 257 spectrophotometer and far IR measurements were carried out on a Beckman IR-12 spectrophotometer. All manipulations were carried out in a dry box under an atmosphere of dry nitrogen.

**Preparation of ligand.** The sodium salt of 5-aminoindazolethiocarbamate was prepared in good yield by reaction of appropriate quantities of 5-aminoindazole, carbon disulphide and sodium hydroxide (7). It was dried in vacuum first at room temperature and then at  $120^\circ\text{C}$  for 24 hr until its infrared spectrum showed no evidence of water of crystallization.

**Preparation of the complexes.** The general procedure employed for the preparation of the complexes is presented first, followed by a summary of the details of preparation of each complex and their yield, which vary from one complex to



the next. A 100 cm<sup>3</sup> solution of anhydrous ligand (4.3 g, 20 mmole) in dimethylformamide (DMF) was added with stirring to the solution of 10 mmole of metal tetrahalide in 100 cm<sup>3</sup> alcohol or chloroform (only for tin(IV) iodide). The solution immediately turned dark brown. This solution was allowed to reflux for six hours and then heated on a water bath to reduce the volume (approximately to 1/3). In every case a solid appeared which was filtered and purified by washing with alcohol or chloroform depending upon which solvent was used for the preparation of the metal halide solution, followed by DMF and lastly with water. It was then washed with ether. The complexes were dried for 24 hours in vacuum desiccator at room temperature then at 120°C for six hours. The amount of metal tetrahalide used in the preparation and yield of complexes are summarized below.

Complex	Metal Halide cm <sup>3</sup> (g)	Yield g (%)
Sn(5-Aidtc)Cl <sub>3</sub>	1.1 (2.6)	3.03(70)
Sn(5-Aidtc)Br <sub>3</sub>	1.3 (4.4)	4.24(75)
Sn(5-Aidtc)I <sub>3</sub>	* (6.3)	5.09(72)
Zr(5-Aidtc) <sub>2</sub> Cl <sub>2</sub>	* (2.3)	4.04(70)
Ge(5-Aidtc) <sub>2</sub> Cl <sub>2</sub>	1.1 (2.1)	4.19(75)
Ti(5-Aidtc) <sub>2</sub> Cl <sub>2</sub>	1.1 (1.9)	4.17(78)

\* These metal halides were solids.

## RESULTS AND DISCUSSION

New dithiocarbamates of germanium(IV), titanium(IV), zirconium(IV) and tin(IV) of the type SnX<sub>3</sub> (C<sub>8</sub>H<sub>6</sub>N<sub>3</sub>S<sub>2</sub>) and MCl<sub>2</sub> (C<sub>8</sub>H<sub>6</sub>N<sub>3</sub>S<sub>2</sub>)<sub>2</sub> (where X = Cl, Br or I; and M=Ge, Ti or Zr) have been prepared in good yield by the reaction of respective anhydrous metal halides with 5-Aidtc. Satisfactory elemental analyses data were obtained for all new complexes. All the complexes formed are thermally stable and are not hydrolysed on exposure to air/water. The complexes were insoluble in all common organic solvents. The compositions of the complexes were established on the basis of their elemental analyses. The coordination mode and stereochemistry was predicated on the basis of infrared spectral

Table 1. Important IR frequencies of the ligand and the complexes and their assignment.

Complex	$\nu(\text{C}^{\bullet\bullet\bullet}\text{S})$	$\nu(\text{C}^{\bullet\bullet\bullet}\text{N})$	$\nu(\text{M-S})$	$\nu(\text{M-Cl})$
Na(5-Aidtc)3H <sub>2</sub> O	1000 vs	1506 vs	-	-
SnCl <sub>3</sub> (5-Aidtc)	1010 s	1510 s	390 vs	390 s, 250 m
SnBr <sub>3</sub> (5-Aidtc)	1015 vs	1408 m	380 s	270 w, 180 m
SnI <sub>3</sub> (5-Aidtc)	1020 vs	1406 m	370 vs	190 m
ZrCl <sub>2</sub> (5-Aidtc) <sub>2</sub>	1020 s	1506 m	385 s	360 s
GeCl <sub>2</sub> (5-Aidtc) <sub>2</sub>	1005 s	1505 m	395 s	430 s, 400 w
TiCl <sub>2</sub> (5-Aidtc) <sub>2</sub>	1015 s	1506 m	375 m	330 s, 350 m

s = Strong, vs = Very Strong, m = Medium and w = Weak



measurements. The infrared spectra were run in KBr in the range 4000-100  $\text{cm}^{-1}$  (Table 1). The infrared spectrum of the ligand has been discussed previously (7).

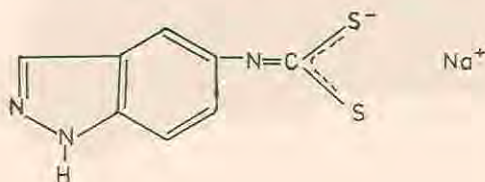
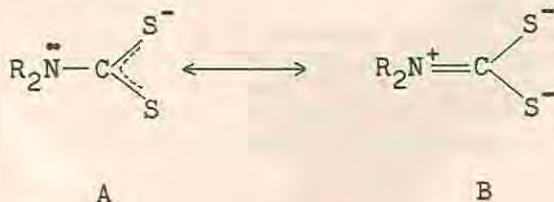


Fig. 1. Na 5-Aidtc

The ligand (Fig. 1) has three coordination sites viz., sulphur (dithio group), amino nitrogen and pyrazole nitrogen. The dithiocarbamate group may act as a unidentate or bidentate ligand. The two bonding possibilities can be distinguished by infrared spectroscopy. The presence of only one strong band in the region  $1000 \pm 70 \text{ cm}^{-1}$  strongly supports chelation of a dithio ligand, a doublet being expected in the unchelated dithiocarbamates (6). Complexes having both monodentate and bidentate dithiocarbamate ligands exhibit additional infrared bands not found for complexes having only bidentate ligands. The more significant of these extra bands are a second ( $\text{C}^{\text{---}}\text{N}$ ) stretching (17) and a second ( $\text{C}^{\text{---}}\text{S}$ ) band (6). However, the splitting of  $\text{C}^{\text{---}}\text{S}$  band may either be due to unidentate behaviour of the ligand or due to the presence of both coordinated and uncoordinated dithiocarbamate group or due to small crystal field splitting (6). All the complexes except the tin complexes, showed a strong band near  $1000 \pm 70 \text{ cm}^{-1}$  which is attributed to  $\text{C}^{\text{---}}\text{S}$  and suggests coordination through sulphur. The tin complexes showed a small splitting or a shoulder in addition to the strong band near  $1000 \pm 70 \text{ cm}^{-1}$  which seems to be due to crystal field splitting (6). However this small splitting of the ( $\text{C}^{\text{---}}\text{S}$ ) band does not indicate the presence of monodentate dithiocarbamate.

The other group through which coordination can occur is the thioureide ( $\text{C}=\text{N}$ ) group. In all these complexes there is a strong band near  $1500 \text{ cm}^{-1}$ . The  $\nu$  ( $\text{C}=\text{N}$ ) values of these complexes are at lower frequencies than  $\nu$  ( $\text{C}^{\text{---}}\text{N}$ ) of the dialkyldithiocarbamate metal derivatives (2). All the complexes showed a strong band in the region  $1505\text{--}1490 \text{ cm}^{-1}$  attributed to the  $\text{C}^{\text{---}}\text{N}$  stretching mode. The structure of the dithio complexes can be represented by the following formulation.

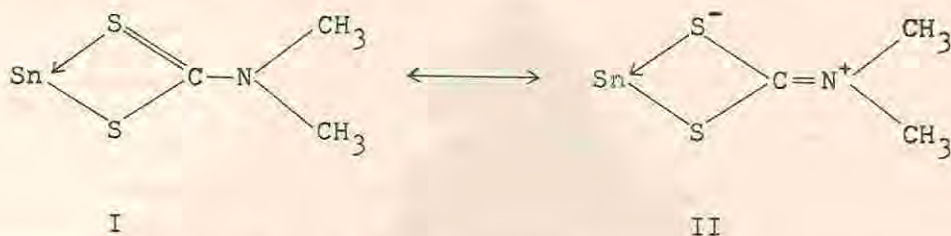


(R = Alkyl or Aryl group)

Chatt and coworkers (18) concluded that the resonance form B contributes to a considerable extent to structure and properties of the dithio complexes. The  $\text{C}^{\text{---}}\text{N}$  band is very sensitive to the substituents on the metal atom, moving to a higher frequency by the introduction of more electronegative substituents. Lower electron density on the tin atom (and thus greater contribution of the



following canonical structure 2) causes comparatively greater double bond character in the (C<sup>≡</sup>N) bond.



Inconsistent with the trend of C<sup>≡</sup>N stretching frequency, the C<sup>≡</sup>S bands move to lower frequency, with increasing electronegativity of the substituents. There is not much difference between the frequency of C<sup>≡</sup>N in the ligand and in the complexes, which does not support the coordination through this group. As explained above, it may be attributed to the less double bond character of C-N bond. The complexes do not show any band at 3400 cm<sup>-1</sup> and 1550-1615 cm<sup>-1</sup> (region for H-O-H and O-H bands), which indicates that the complexes are free of water of crystallization. Far IR spectra were recorded to obtain a more decisive evidence about the steric configuration of these complexes. The  $\nu$  (M-X) usually appears as a strong band and shifts to lower frequency with increasing size of the halogen. The close similarity between the spectra of SnX<sub>3</sub>(5-Aidtc) and MCl<sub>2</sub>(5-Aidtc)<sub>2</sub> in the (M-X) region indicates a similar environment in both types of complex, thereby ruling out the possibility of 5-coordinated metal in the case of MX<sub>3</sub>(5-Aidtc) complexes (17). To account for the stoichiometry required for an octahedral structure, the sixth site must be occupied by a bridged ligand or a halogen molecule.

The far IR spectra of the new dithiocomplexes have been investigated. In all cases there is a band in the 370-390 cm<sup>-1</sup> region which is absent in the spectra of the ligand. It is tentatively assigned to  $\nu$  (Sn-S) stretching mode (19-20). The frequency shifts of this band caused by substituents on the metal show the same tendency as the (C<sup>≡</sup>N) stretching frequency. Absence of (M-N) bands from the spectra rules out the possibility of coordination through nitrogen.

In the SnCl<sub>3</sub>(5-Aidtc) and SnBr<sub>3</sub>(5-Aidtc) complexes two bands of varying intensity i.e. a strong and a weak band were observed in the 370-390 cm<sup>-1</sup> region. These bands are attributed to terminal and bridging halogens. The bridging  $\nu$  (Sn-I) could not be detected in SnI<sub>3</sub>(5-Aidtc) complex because it falls below the range of spectra taken, so the sixth site in tin complexes is satisfied by bridging halogen. A polymeric structure involving halogen bridging, and an octahedral geometry of metal is proposed for the tin complexes. A single  $\nu$  (M-Cl) band in ZrCl<sub>2</sub>(5-Aidtc)<sub>2</sub> is suggestive of *trans*-octahedral geometry. In TiCl<sub>2</sub>(5-Aidtc)<sub>2</sub> and GeCl<sub>2</sub>(5-Aidtc)<sub>2</sub> two  $\nu$  (M-Cl) bands are found in the far IR region which are attributed to the *cis* halogens. Therefore, a *cis*-octahedral structure is proposed for these two complexes.

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