

Synthesis & Characterisation of Ge(IV), Sn(IV), Ti(IV) & Zr(IV) Complexes of 5-Aminoindazolyl Dithiocarbamate

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Received 13 November 1984; revised and accepted 7 May 1985

The synthesis and characterisation of 5-aminoindazolyl dithiocarbamates of Ge(IV), Sn(IV), Ti(IV) and Zr(IV) are described. The results of IR analysis of the complexes indicate octahedral structures in which two of the dithiocarbamate moieties are bound symmetrically and two others unsymmetrically to the metal ions.

Indazoles and substituted indazoles have been used as corrosion inhibitors, in the preparation of different types of dyes¹⁻³ and as complexing agents⁴. The title investigation is in continuation of our studies on metal dithiocarbamates⁵⁻⁷.

Tin(IV) halides were prepared according to the standard methods and GeCl₄(Koch-Light), ZrCl₄, TiCl₄(BDH) and 5-aminoindazole (Koch-Light, m.p. 175°C) were used as such. The solvents were purified by conventional methods. The infrared spectra in the range 600-4000 cm⁻¹ were recorded in KBr matrix and in the range 200-600 cm⁻¹ as nujol mull on a Perkin-Elmer 621 spectrophotometer.

Preparation of complexes

5-Aminoindazolyl dithiocarbamate (0.1 mol) dissolved in dimethylformamide was added dropwise with continuous stirring to metal tetrahalide (0.025 mol) solution in ethyl alcohol or chloroform. The

reaction mixture was heated on a water-bath and the resulting precipitate filtered, washed with ethanol and dried *in vacuo*.

The analytical data are presented in Table 1. All the compounds are high melting or decompose on melting. Due to their insolubility in organic solvents, the conductivity measurements could not be carried out.

There are two possibilities of formation of metal(IV) dithiocarbamates (see structures I and II). That the dithiocarbamates are formed via the ligand structure(I) is supported by the IR data.

In the IR spectrum of aminoindazole, the $\nu C-N$ mode appears as a split band at 1352 and 1323 cm⁻¹. The bands appearing in the region 370-395 cm⁻¹ in all the complexes have been assigned to $\nu(M-S)$. The band at 1643 cm⁻¹ has been assigned to the ring vibration. The bands at 1000 and 1460 cm⁻¹ in the ligand are characteristic of $\nu C-S$ and $\nu S-C-N$ respectively. Since the aminoindazole is a closed ring system it decreases the delocalization of electrons over the dithiocarbamate group which is reflected by the decrease in $\nu C=N$ modes as compared to that of alkyl dithiocarbamates⁸.

Following the criterion of Bonati and Ugo⁹, it is possible to assign the characteristic $\nu S-C-N$ and $\nu C-S$ modes with certainty, and a distinction between a symmetrically and an unsymmetrically bound dithiocarbamate moiety can be made. The presence of

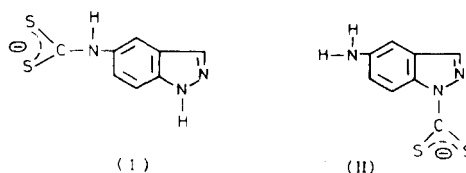


Table 1—Analytical Data of 5-Aminoindazolyl Dithiocarbamate Complexes

Complexes	Colour	m.p. °C	Found (Calc), %				
			C	H	N	S	M
5-Aldtc Na3H2O	Dark pink	350 ^d	33.68 (33.43)	4.21 (4.32)	14.73 (14.50)	21.18 (22.45)	
Sn(5-Aldtc) ₄	Light brown	240 ^d	40.39 (40.19)	2.52 (2.58)	17.67 (17.76)	26.92 (27.06)	12.48 (12.42)
Zr(5-Aldtc) ₄	Pink	285 ^d	41.59 (41.71)	2.59 (2.64)	18.19 (18.25)	27.73 (27.88)	9.88 (9.94)
Ge(5-Aldtc) ₄	Brown	270	42.44 (42.38)	2.65 (2.67)	18.57 (18.45)	28.29 (28.35)	8.02 (7.93)
Ti(5-Aldtc) ₄	Dark brown	185 ^d	43.64 (43.82)	2.72 (2.69)	19.09 (19.18)	29.09 (29.24)	5.44 (5.48)

d = Decomposition temperature.

only one band in the region $1000 \pm 70 \text{ cm}^{-1}$ is indicative of a chelated dithiocarbamate group while splitting of this band suggests unsymmetrical behaviour of dithiocarbamate growth. In the IR spectra of the present complexes, two bands appear in the region $1065\text{--}990 \text{ cm}^{-1}$. One of the bands may probably be due to $\nu\text{C}=\text{S}$ while the other one may be a combination of the split bands¹⁰. In view of the splitting of $\nu\text{C}-\text{S}$ it is possible that two of the four dithiocarbamate groups in $\text{M}(\text{dtc})_4$ are symmetrically coordinated while the other two are unsymmetrically coordinated as has been observed in the case of $\text{Pt}(\text{IV})$ and $\text{Sn}(\text{IV})$ dithiocarbamates^{5,11}. Thus it may be proposed that the present complexes may have octahedral structures similar to those of the dithiocarbamate complexes of $\text{Pt}(\text{IV})$ and $\text{Sn}(\text{IV})$.

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